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AN INTRODUCTION TO THE CHEMISTRY OF COLLOIDS.

*A COMPENDIUM OF COLLOIDAL CHEMISTRY FOR
STUDENTS, TEACHERS, AND WORKS MANAGERS.*

BY

DR. VICTOR PÖSCHL

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Translated from the Second, Enlarged, German Edition

BY

HERBERT H. HODGSON, M.A.(CAMB.), B.Sc.(LOND.),
PH.D.(HEIDELBERG),

LECTURER AND RESEARCH CHEMIST AT THE MUNICIPAL TECHNICAL COLLEGE, BRADFORD
LATE MAJOR SCHOLAR OF TRINITY COLLEGE, CAMBRIDGE, AND BRADFORD
CITY COUNCIL TRAVELLING SCHOLAR.



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INTRODUCTION.

UNTIL a few years ago the Colloids obtained but little recognition in General and Inorganic Chemistry, being infrequently, and then only imperfectly, mentioned.

A chemist, realising the importance of Colloidal Chemistry and desiring to become better acquainted with this interesting chapter of science, must have recourse to the whole of the special literature of the subject, a matter not always possible, and there has been no short compendium of the subject.

The Author endeavours to remedy this in the present volume, and aims at giving in concise form a review of the present position of the colloid problem, which will, it is hoped, meet the requirements of students of chemistry, pharmacy, &c., who desire to obtain the most essential knowledge concerning colloids.

In addition, it will serve as a short manual for technologists, works managers, lecturers, and others who have not had opportunity of making acquaintance with this most recent development of science, which is undoubtedly of increasing importance.

CONTENTS.

	PAGE
I.—GENERAL CHARACTERISTICS. NOMENCLATURE, . . .	1
II.—PROPERTIES OF COLLOIDAL SOLUTIONS, . . .	6
Density. — Osmotic Pressure. — Diffusion. — The Brownian Movement.—Optical Properties.—Elec- trical and Magnetic Properties—Cataphoresis.— Transformations—Properties of the Jellies.	
III.—THE RELATION OF COLLOIDAL SOLUTIONS TO SOLUTIONS PROPER AND TO SUSPENSIONS, ✓	20
IV.—THE DISPERSOIDS AND THEIR CLASSIFICATION, . . .	28
General Classification.—Suspension and Emulsion Colloids.	
V.—PREPARATION OF COLLOIDAL SOLUTIONS,	32
Summary of Matter known in Colloidal and Crystal- loidal States.—Methods for the Preparation of Colloidal Solutions.	
VI.—RESEARCH METHODS. ULTRAMICROSCOPY,	71
VII.—RECENT VIEWS ON THE NATURE OF THE COLLOID STATE,	80
The Solution Theory.—The Adsorption Theory.— The Suspension Theory.—Crystalline Theory.	
VIII.—THE IMPORTANCE OF COLLOIDAL CHEMISTRY TO OTHER SCIENCES,	97
Mineralogy.—Agriculture.—Medicine.	
IX.—THE IMPORTANCE OF COLLOIDAL CHEMISTRY IN CHEMICAL INDUSTRY AND TECHNOLOGY, . . .	102
X.—LITERATURE OF THE SUBJECT,	106
INDEX,	109

CHEMISTRY OF THE COLLOIDS.

I. General Characteristics. Nomenclature.

DURING his researches into the nature of the diffusion of dissolved substances, Thomas Graham found that certain bodies, especially those which crystallise with ease from their solutions, rapidly diffuse from their solvents into pure water or pass through animal membranes, while, on the other hand, amorphous matters retain their union with the solvent to a certain degree of tenacity, and exhibit a marked deviation in their properties from the first-named substances. In order to differentiate between crystalloidal substances and those bodies diffusing with difficulty, and of which glue (*κόλλα*) may be regarded as typical, he proposed for the latter the term "colloidal substances." Graham may be rightly considered as the investigator who laid the foundations of colloidal chemistry by means of his two fundamental works, which,

appearing in 1861 and 1864, contained the first comprehensive notice of the colloids.

The dissimilarity between the two classes named afforded to Graham, not only a means for their separation, but also a method for the preparation of pure colloids. If a layer of water be placed carefully over another containing both colloidal and crystalloidal substances in solution, then after a short interval part of the crystalloids will diffuse into the aqueous stratum above, while the colloids remain behind. This diffusion may take place through a partition composed of gelatinous material, and the resulting separation was termed by Graham "Dialysis." Animal membranes, and also suitable parchment paper (vegetable parchment), are used as dialysing partitions. The vessel known as the dialyser is closed at the base by the membrane and immersed in pure water. The process of diffusion through membranes is termed Osmose. As an example of dialysis, the case of a water solution containing gelatine, common salt and sugar may be cited; the two latter substances diffuse through the membrane as crystalloids, the gelatine remains behind as a colloid.

In addition to glue, which has already been mentioned, the following are recognised colloids:—Starch, dextrine, varieties of gum, albumen, caramel,

tannins, caoutchouc, resin, and numerous other animal and vegetable substances. Among inorganic bodies the aqueous solutions of many acids, oxides, and salts, such as silicic, stannic, and tungstic acids, alumina, iron oxide, etc., may be mentioned. According to recent research the sulphides of the heavy metals are colloids, in addition to several metals and many inorganic and organic salts. A survey of substances known in the colloidal state is contained in Chapter v., p. 33.

Many bodies usually regarded as insoluble in water, such as silicic acid, ferric hydrate, arsenic trisulphide, appear to dissolve under certain conditions, a fact observed about the middle of the last century. If the solutions named be submitted to dialysis, they are shown to be "colloidal." For example, if a concentrated solution of an alkali silicate be mixed with hydrochloric acid, then silicic acid separates as a friable, gelatinous mass. If, however, the solutions employed be dilute and excess of acid used, no precipitation takes place, the solution remaining clear and apparently unchanged. On the surface it seems as if silicic acid were sparingly soluble, and, therefore, will partially separate from concentrated solutions while remaining dissolved in excess of water. This, however, is not the case; for the solution of silicic acid

which arises is not a true solution, but a "pseudo solution," in which silicic acid is present in the colloidal state, a fact easily verified by dialysis. This colloidal solution when dried forms an amorphous, vitreous mass, which cannot again be completely dissolved in water.

Graham has further discovered that, not only is water capable of forming colloidal solutions, but that other liquids, such as alcohol, benzol, glycerine, and even sulphuric acid, possess this property; he designates colloidal solutions as sols, in particular aqueous solutions as hydrosols, alcoholic as alcosols, glycerine as glycerosols, etc.; those sols, whose solvent is of an organic nature, are at present usually termed organosols.

Since Graham, a number of authors* have described the properties and conditions of existence of many new colloids, yet even now the question as to the nature of the colloidal state remains open. At the present time we know that colloidal solutions, the most important element in colloidal formation, consist of at least two varieties of spatially separated matter: of a liquid and of another finely divided solid or liquid substance in the same. These

* An excellent account of the History of Colloidal Chemistry is given by Wo. Ostwald in *Grundriss der Kolloidchemie*. (Dresden, 1909.)

sharply separated components of the sol are termed phases in the physico-chemical sense. In colloidal solutions we have presented to us a many-phased, heterogeneous structure. As essential properties of the same we have to emphasize two important criteria—viz., that the one phase is extraordinarily finely divided, and, therefore, presents an enormous development of surface to the second phase. The distribution of the phases is, moreover, so uniform that the sols appear entirely homogeneous to the naked eye. Many colloids however, as for example the gels, do not exhibit the usual discernible homogeneity if they have been caused to swell or have been formed by coagulation. In such cases an heterogeneity may be observed more or less clearly by the naked eye—*i.e.*, macroscopically—and the system concerned is therefore designated macroheterogeneous. For those colloidal heterogeneous structures, the sols, which principally interest us, other expressions are used; the term “microheterogeneous” (G. Bredig) clearly denotes that the heterogeneity may only be perceived on strong magnification. Equally important also is the expression “disperse heterogeneity” (Wo. Ostwald); P. P. von Weimarn proposes the general term “dispersoids,” and Wo. Ostwald “disperse heterogeneous systems.”

That phase, the total mass particles of which are in contact, is called the "dispersion medium," while the phase consisting of isolated particles is known as the "disperse phase."

There are colloids, however, of which the structure differs from those just described in that the disperse phase forms a network, similar to the fibrous frame of a bath sponge or a system of rafters, through which the dispersion medium permeates.

The state of division of the disperse phase may, obviously, be very different, and is expressed by the degree of dispersion or of colloidal refinement.

II. Properties of Colloidal Solutions.

1. Density.

The density of colloidal solutions cannot be calculated from the densities of the disperse phase and the dispersion medium—it is usually greater than the number obtained by calculation. The dispersoids, in other words, exhibit a volume contraction, in contrast to simple mechanical mixture. This fact is clearly indicated when the following numbers are compared. They show the volume of gelatine solution which may be obtained from one cubic centimetre of water :—

With 10 per cent. gelatine the volume amounts to 0.96069 c.c.

„ 25	„	„	„	„	0.93748 „
„ 50	„	„	„	„	0.90201 „

Other examples may be quoted showing the density of bodies to increase with progressive division. G. Rose found the following characteristic numbers for different states of gold :—

For gold, molten and pressed into plates, D (density)	=	19.33
„ precipitated by oxalic acid, D	.	. = 19.49
„ „ as the finest powder by ferrous sulphate, D	.	. = 19.55-20.71
For pure heavy spar (Barytes), D	.	. = 4.48
For precipitated Barium sulphate, D	.	. = { 4.521 and 4.535

2. Osmotic Pressure.

The osmotic pressure of colloidal solutions is very small, in many cases too minute for observation. This fact is in accordance with a theory mentioned earlier (*vide* pp. 4, 5, and 6), according to which the disperse phase is distributed throughout the liquid as fine particles.

The observed elevation of the boiling point, together with the depression of the freezing point, should really be evidence that hydrosols are true solutions, facts which will receive consideration when reviewing the solution theory. The small deviations observed, however, have no intrinsic value, since traces of impurity and errors of observation may exert an influence on the final result

that is indeterminable. At this stage the fact may be mentioned that colloidal matter behaves differently in different dispersion media. For example, E. Paterno noticed that tannic and gallic acids exhibit no depression of the freezing point with water as solvent, while with glacial acetic acid the deviation corresponding to the molecular weight was given. It follows, therefore, that the colloid does not dissolve in water, but is engaged in swelling. Generally, it may be accepted that the freezing and boiling points of hydrosols show an extremely small deviation from the corresponding fundamental points of water.

3. Diffusion.

As Graham supposes (*vide* p. 1), only crystalloidal substances possess the common property of diffusion, a fact which can be used for their separation from colloids. According to the investigations of H. Leplay, and in addition of W. Meyer and Eykmann, certain sols are able to diffuse through parchment. Accordingly, the distinction between colloids and crystalloids lies only in their velocities of diffusion. This analogy becomes clear when one considers that the dispersoids are only differentiated by their degree of dispersion. The further peculiarity is then intelligible—viz., that the solid particles of

real suspensions diffuse, even if slowly and to a small degree, into a pure liquid.

4. The Brownian Movement.

The particles of the disperse phase are engaged in a peculiar vibratory motion in the liquid, which R. Zsigmondy describes as like "dancing, hopping, jumping"; this motion was named "the Brownian movement," after its discoverer, the botanist R. Brown (1827). It takes place mostly about a fixed mean position, the motion being rarely translatory. The smaller particles in particular are engaged in zig-zag vibrations, the larger, however, move with less celerity. Particles whose diameter exceeds 3 to 5 μ^* do not exhibit this movement. The vibration is influenced by the concentration of the particles, and also by the viscosity of the liquid; should the tenacity of the liquid be not too great, the Brownian phenomenon may generally be observed, obviously, however, when the size of the particles falls below the limit given above. The chemical and physical nature of the disperse phase is usually without influence on the movement (without regard to the velocity), as also the effect of long-continued boiling or alterations in illumination and temperature.

* 1 μ (micron) = 0.001 mm.

To account for the Brownian movement different theories have been put forward, without, however, affording entire satisfaction. The most acceptable is one which supposes internal heat energy to be the cause of the vibration.

Without going deeply into the theoretical aspect of the above phenomena, an indication at least may be given as to how the occurrence of the Brownian movement in colloidal solutions may be explained. In every disperse system the density of the disperse phase differs from that of the dispersion medium. Nevertheless, gravitation only operates to form a scum or a sediment when the particles exceed a definite magnitude (on the average 0.1μ). We must regard particles in suspension as characteristic of colloidal and molecular solutions. Suspension is most uniform in crystalloidal solutions—*e.g.*, in a common salt solution—for on changing the concentration, for example, by abstracting the solvent through diffusion, a state of equilibrium will be gradually attained once more. Diffusion of the dissolved body operates as it were in opposition to gravity; nevertheless, we must assume the particles of the salt to have a higher density than pure water. That the salt does not sink to the bottom is due to the viscosity of the water, which cannot be overcome by the weight of particles

whose magnitude falls below a certain limit. The dissolution of common salt proceeds by the water continuing to separate the smallest particles from the surface of the salt and involve them intimately with the liquid, until a state of equilibrium is arrived at. The latter, however, is only possible when all the particles are at an equal distance apart—*i.e.*, when the concentration is uniform at every point. The viscosity probably assists to obtain the condition by working in opposition to gravitation, the latter force not gaining the upper hand owing to the smallness of the particles; the particles themselves move only a little, if at all, from the equilibrium position into which they have been brought by the viscosity. Crystalloidal solutions behave in this way when the disperse particles are larger, as in the case of colloidal solutions, gravitation works more powerfully against viscosity; the particles are drawn downwards or upwards with greater intensity, and displaced as far as the viscosity of the dispersion medium allows, from which they oscillate back to the position of rest. Viscosity and gravitation strive then for possession of the particles, thereby causing the latter to oscillate about a fixed mean position—*i.e.*, they take part in the Brownian movement.

If the particles are still larger, we have the case

of coarse suspension, where gravitation gains the upper hand and the particles either rise to the surface or sink downwards. The former case is that of scum or cream formation (*e.g.*, in fresh milk where the drops of butter fat have diameters from 2 to 10 μ), the latter that of sedimentation (*e.g.*, starch production).*

5. Optical Properties.

Many hydrosols appear clear and homogeneous to the naked eye ; heterogeneity is mainly recognised by turbidity, fluorescence, and opalescence. Generally the Tyndall effect may be observed. If a beam of light be passed through a colloidal solution, the light is repeatedly reflected by the disperse particles, thereby being scattered and polarised. The Tyndall effect is the basis of ultramicroscopy, a subject more fully discussed in Chapter vi. (p. 71), The principle of this research method consists in the fact that if an intense beam of light be passed through a colloidal solution, the light is diffracted by the disperse particles. In this way a diffraction patch arises which may be seen through the microscope.

The colour of colloidal solutions having a liquid

* The smallest particles of fine-grained starch—viz., rice starch—are 2 μ in size ; the grains of potato starch attain a length of 100 μ .

disperse phase is usually insignificant, varying from white to yellow. In contrast to this, metallic hydrosols exhibit beautiful colours and of which many examples (*vide* p. 53) will be given later.

6. Electrical and Magnetic Properties—Cataphoresis.

ELECTRIC CHARGE.—The disperse phase is charged with positive or negative electricity. The following are examples of colloidal solutions :—

(a) With a positive charge—Metallic hydroxides, silicic acid, and basic dyes, such as methyl violet, methylene blue, and magdala red.

(b) With a negative charge—All the metals, metallic sulphides, dyes such as aniline blue, indigo, methylaniline green, eosine, fuchsin, mastic, gamboge, and starch.

The fixed sign of the charge is only true for water as dispersion medium. Colloidal solutions in turpentine have a charge of opposite sign. The nature of the charge varies, therefore, with the fluid used as dispersion medium; indeed, the discharge of the sols has been affected by the addition of suitable dispersion media. For example, W. B. Hardy succeeded in proving that albumen solutions may be negatively charged by the addition of small quantities of alkali, and positively when acidified. The

electric charges carried by colloidal solutions having a liquid disperse phase are essentially smaller.

CATAPHORESIS.—If an electric current be passed through a colloidal solution which is as free as possible from electrolytes, a movement of the disperse phase takes place, in a direction depending on the sign of the charge; the positively charged phase moves towards the cathode, the negative to the anode. On analogy with osmotic phenomena (which take place through membranes) this movement is named “Electric Osmose” or “Cataphoresis.” The velocity with an E.M.F. of 1 volt per cm. is $(2 - 4) \cdot 10^{-4}$ cm. (The Svedberg)—*i.e.*, about a hundred times as small as the Brownian movement. Cataphoresis is influenced by the addition of free ions.

ELECTRIC CONDUCTIVITY.—Colloidal solutions conduct electricity considerably less than dissociated solutions.

MAGNETIC PROPERTIES.—Colloidal solutions, whose disperse phase when in the natural state exhibits magnetic properties—*e.g.*, iron and nickel—are distinctly magnetic.

7. Transformations—Properties of the Jellies.

A special feature of colloidal solutions is that by mechanical means, or on heating, the dissolved

substance separates in an insoluble form ; on increasing the concentration either spontaneously or by the addition of certain bodies (*e.g.*, electrolytes) they are transformed into jellies or precipitated (from dilute solutions) generally in an insoluble condition. Graham has termed the insoluble body which separates, a gel ; should such a jelly arise from an hydrosol and retain water, it is known as an hydrogel ; the process of gel formation has been named pectisation, coagulation, precipitation, or flocculation. Water may be completely expelled from an hydrogel by means of alcohol, concentrated sulphuric acid, etc., the resulting gel being termed alcogel, sulfogel, etc., respectively.

All aqueous solutions on coagulation are not homogeneous ; some leave behind an aqueous residue, others an insoluble one. On account of this property the hydrosols have been classified by W. B. Hardy, with suitable limitations, as reversible and irreversible, according to whether the dried residue is soluble or insoluble in the solvent employed. Among those hydrosols classified as reversible colloids are aqueous solutions of gelatine, glue, gum, molybdenum blue, tungstic and molybdic acids, etc. ; as irreversible are solutions of colloidal stannic acid, ferric oxide, alumina, arsenic trisulphide, gold, silver, platinum, etc. When these

are present in a sufficient state of purity and free from certain reversible organic colloids, known as protective colloids, since by the addition of these to irreversible colloids the latter are transformed into reversible.

This division characterises the differences between the two groups. While the reversible hydrosols are often almost insensible to the addition of electrolytes, the irreversible, as a rule, prove extremely sensitive, coagulation being caused by the presence of very minute quantities—*i.e.*, the irreversible hydrosol changes into an hydrogel, or separates from the liquid in a gelatinous or amorphous condition. Reversible hydrosols are easily prepared by dissolving the solid colloid in water, while the preparation of irreversible hydrosols is only possible by indirect means, on account of their insolubility in the dry state.

By suitable precipitating agents the colloid can often be separated from the hydrosol, so as not to lose its capability of again forming an hydrosol with pure water. Lottermoser proposes the terms solid and liquid hydrosol, and distinguishes as hydrogel the insoluble amorphous body; only the solid hydrosol, and not the hydrogel, may be converted into a fluid form.

Electrolytes only cause the coagulation of colloidal

solutions, if their concentration exceeds a certain minimum value, which has been termed the coagulation point (Schwellenwerte). Below this value, lapse of time produces no change. H. Schulze * has proved in the case of arsenic trisulphide hydrosol that equal quantities of different precipitating salts produce varying coagulation effects. This fact is expressed by the table showing the molecular precipitating capacity of electrolytes. The latter value is the reciprocal of the number of gramme molecules contained in one litre of the liquid. If KI be chosen as fundamental unit, then the following numbers are obtained :—

KCl,	2·5
Na ₂ SO ₄ ,	2·5
CaCl ₂ ,	80·0
MgCl ₂ ,	182·0
ZnSO ₄ ,	60·0
Al ₂ Cl ₆ ,	1518·0
Al ₂ (SO ₄) ₃ ,	957·0

In the case of arsenic sulphide hydrosol the coagulating effect of an electrolyte is dependent on the valency of the kation, not of the anion. This result has been confirmed by other investigators for different sols (of the sulphides and metals). For positively charged colloids the precipitation

* *Journ. f. prakt. Chem.*, xxv., 431 ff (1882). Compare A. Müller, *Allg. Chemie der Kolloide*. (Leipzig, 1907.)

effect of electrolytes depends on the valency of the anion, not of the kation.

Coagulation by electrolytes is usually accompanied by colour changes of the sols, examples being given later (*vide* p. 40).

Inorganic hydrosols may be protected against the precipitating action of electrolytes by the addition of organic colloids. Such colloids, which are able to protect others, are termed "Protective colloids." The protective effect is expressed after R. Zsigmondy by the so-called "gold value." As experimental liquids, a gold sol having 0.0053 to 0.0058 per cent. of gold, and a sodium chloride solution containing 100 grs. common salt in 900 c.c. water are taken. The gold value of a colloid is the number of milligrammes of this colloid which are just capable of protecting 10 c.c. of the above gold solution from coagulation by 1 c.c. of the given common salt solution. For comparison the gold values of several colloids used in manufacture are appended :—

Gelatine,	0.005 to 0.01
Russian glue,	0.005 „ 0.01
Cologne glue,	0.005 „ 0.01
Isinglass,	0.01 „ 0.02
Egg albumen,	0.15 „ 0.25
„	(another sample),	0.1 „ 0.2

Gum arabic (first sample), . . .	0.15 to 0.25	
„ (second sample), . . .	0.1	
„ (third sample), . . .	0.5	„ 4
Caragheen,	0.5	„ 1
Dextrine,	6	„ 12
„ (another variety), . . .	10	„ 20
Wheat starch,	about 4	„ 6
Potato starch,	about 25	

The law governing the mutual precipitation of colloidal solutions may be summed up in the sentence that sols containing opposite charges precipitate each other, those with similar charges do not. Precipitation stands, therefore, in intimate connection with the electrical properties. The latter is one of the most important results gained by investigation into the nature of colloids, and is of far-reaching importance industrially (dyeing, etc.).

PROPERTIES OF JELLIES.—Jellies obtained by coagulation may be regarded as colloidal solutions in which the disperse phase appears in a higher state of concentration. That the jellies should exhibit certain properties of solid bodies now becomes clear. They may take a definite external form—*e.g.*, a piece of swollen glue. Jellies which have resulted from sols whose disperse phase is liquid generally prove to be elastic (caoutchouc). Molecular and colloidal solutions can diffuse through

jellies, this process being more energetic the smaller the concentration of the jelly's disperse phase. This prevents the normal process of chemical action, such as takes place in solution when a precipitate forms by intimate admixture, and causes peculiar precipitate patterns to arise, as, for example, the Liesegang stratification figures (Liesegangschen Schichtungsfiguren).

x x x x

III. The Relation of Colloidal Solutions to Solutions Proper and to Suspensions.

We will now consider somewhat more thoroughly the relationship between colloidal and crystalloidal solutions.

As already described, the general characteristics of the latter are the ability to diffuse, osmotic pressure, capability of the dissolved (solid) body to crystallise from saturated solutions. The question arises whether mixtures which lack the characteristics mentioned (colloidal solutions or hydrosols) may be classed in general as solutions in the sense required by Wilhelm Ostwald and W. Nernst, who define solutions as homogeneous mixtures, or physical mixtures of homogeneous phases. In this definition the criteria mentioned above are not in any way included—*i.e.*, they are not considered—the question

naturally depends on establishing the fact whether colloidal solutions are homogeneous or not. True solutions are homogeneous in as much as they neither separate mechanically into components, nor may any solid particles be recognised by optical methods—*i.e.*, by the naked eye or by means of optical instruments. Many colloidal solutions prove themselves mechanically inseparable, since they pass through filter paper, even if slowly. R. Zsigmondy has been able to filter a colloidal gold solution unchanged through a clay cell. Nevertheless, lack of homogeneity may be proved in colloidal solutions by optical means, using the Faraday-Tyndall cone of light. Earlier, this had been denied by R. Zsigmondy, and later by D. Konowalow, the latter attributing heterogeneity to a partial separation from the rest of the homogeneously dissolved body, the former regarding lack of homogeneity as accidental. Meanwhile the assumption of heterogeneity has been well established, and the significance ascribed to it by M. Faraday, H. Picton and S. E. Linder, W. Spring, G. Bredig, etc., will be dealt with later.

Since the discovery of the ultramicroscope we have been able to decide between homogeneity and lack of it, with much greater certainty than was formerly possible.

Through the methods worked out by R. Zsigmondy and H. Siedentopf, and to be described later, we have been able to orientate more exactly the cause of heterogeneity. We now know that liquids containing particles of $20\ \mu\mu$ ($1\ \mu\mu = 0.000001\ \text{mm.}$) appear clear, and that turbidity first ensues only when particles of about $100\ \mu\mu$ in magnitude are present. There is thus a possibility of regarding the colloids in some measure as intermediate members between clear homogeneous crystalloidal solutions and coarse mechanical suspensions.

With the development of science many terms, once possessing a definite meaning in relation to others, are retained, but have since become inaccurate. This has taken place in our case. Graham was not conscious of the possibility of connecting links between two groups of bodies when he put forward the idea of colloids in contrast to that of crystalloids. On account of the enormous mass of detail, we must of necessity at the present time narrow the limitations of the above ideas and establish arbitrary divisions, as, for example, in geology, where it has been sought to define quantitatively the ideas concerning rocks, rubble, gravel, sand, loam, and clay.

In my opinion there exists a continuous transition between crystalloidal solutions and suspensions

proper through the province of the colloids ; if in agreement with Bredig one can accept the following characteristics as distinguishing colloidal from crystalloidal solutions, viz. :—Capability of diffusion, work required for the removal of solvent, electrical movement, coagulation, adsorption, irreversible transformations and hysteresis, imperviousness to other colloids, optical heterogeneity, and electrical preparation of sols. Then I believe this to be correct for typical crystalloids and colloids, but in the above distinctions transition stages are not considered, and these undoubtedly exist. If, in addition, crystalloidal solutions prove to be perfectly homogeneous, then it appears to me yet possible that the supposed heterogeneity on the molecular theory of every solution could be established by other methods. A final decision must, however, be suspended until later investigations come to hand.

A work written by R. P. van Calcar and C. A. Lobry de Bruyn throws some light on this interesting question ; these Dutch investigators have been able to effect considerable concentration changes by the use of centrifugal force in salt solutions—*e.g.*, from a saturated solution of Glauber's salt three-eighths of the dissolved salt crystallised on the circumference of the rotating vessel. I am in

agreement with the above authors that typical crystalloidal solutions are not homogeneous in the strictest sense of the word. In order to be able to decide in the best way the earlier problem proposed—viz., whether colloidal solutions may be separated from crystalloidal—we will simply consider as solutions those which appear to be clear by ordinary daylight, and are not divided into their component parts by the customary means of separation (filtration and decantation), since we desire to classify the known heterogeneous appearing substances apart from proper solutions; for not only colloidal, but also numerous crystalloidal solutions—*e.g.*, fuchsin, ferric chloride, chromium chloride, saccharose, and raffinose—are excluded from the rank of true solutions.

The relation of colloidal solutions to suspensions—*i.e.*, to coarse mechanical states of division, will next be taken, and here in the typical representatives of both groups the conspicuous difference in magnitude of the hydrosol particles and such contained in genuine suspensions may be distinguished. In addition, the following features are characteristic of typical colloids in contrast to suspensions:—

1. Irreversible transformations.
2. Changes in the total energy of the system on coagulation.

3. The adsorption of finely divided matter by porous substances, such as charcoal.

4. The ability of colloids to react with each other in a manner strikingly similar to chemical action.

The powder of an almost insoluble body may with ease be stirred with a liquid forming a suspension, but on standing the powder through gravitation separates from the liquid. The powder deposited may be triturated and again sedimented any number of times. In this way only the distances between the separate particles undergo alteration. Addition of electrolytes to coarse suspensions causes no essential change, a fact easily demonstrated by taking a suspension in pure water of potato starch or quartz whose grains are at least 0.06 mm. in magnitude, and allowing it to settle in a dilute solution of common salt. After evaporation of the liquid the powder which has been in suspension may be again triturated. It is otherwise with colloids. If, for example, experiments be made with colloidal gold, which is free from other colloids, to separate it from the liquid in which it is distributed, either by evaporation or by addition of electrolytes, the metal coagulates thereby making it impossible to bring it to its former state by shaking; moreover, it has undergone a colour change (irreversible transformation). There are,

however, numerous transitions from coarse mechanical suspensions to colloidal solutions ; it may be taken for granted that suspension is more like colloidal solution, the finer its state of division. In the case of potato and wheaten starches the influence of the state of division may be easily observed. The larger particles of the former are scarcely affected by electrolytes, while the finer grains of wheaten starch exhibit a distinct flocculation when common salt is added, in addition to an accelerated rate of deposition. Turbidity, due to clay, ultramarine, or the much investigated mastic, afford examples of transition between colloidal solutions and suspensions.

In order to define the limit between colloidal solutions and suspensions, special emphasis must be laid on the fact that in a suspension the suspended matter yields to the pull of gravitation, while in every other finely divided state, including colloidal solutions, this is not the case. The properties of colloids mentioned in pp. 6-12 are for the most part connected with this independence of the particles from the gravitation force. Until about a magnitude of $1\ \mu$ we have coarse mechanical suspensions, from $20\ \mu\mu$ upwards colloidal and apparently homogeneous solutions. Between these limits of division lie the transition forms, which are classified

according to their nature, some with colloidal solutions, others with the finer suspensions. The above appears to me to agree with the earlier mentioned transition, according to their degree of division between crystalloidal solutions, colloidal solutions, and suspensions. As a rule, crystalloidal solutions are regarded as being in the most perfect state of divisibility, colloidal as less complete. The magnitudes of the particles, of which $20\ \mu\mu$ serves as the upper limit in colloidal solutions, by increasingly greater division, are such as cannot be detected even by the ultramicroscope; we may fix $0.1\ \mu\mu$ as approximately the extreme limit of divisibility, and regard this as the upper limit to the absolute size of molecules (or atoms).

The above is in striking agreement with the absolute molecular (or atomic) magnitude derived from the equations of the kinetic theory of gases or by other methods, which latter only allow an upper limit for molecular dimensions to be established. I might here mention that long ago an upper limit for molecular magnitude had been sought from considerations of the intensity of dye solutions, as well as from perceptions of odour. A. W. Hofmann found that dyes, such as fluorescein, etc., are still visible when diluted more than a million fold. Berthelot observed that a hundred

billionths of a gramme of iodoform could still be scented. Bunsen and Kirchhoff discovered that $\frac{1}{3} \cdot 10^{-6}$ mg. of NaCl could be detected by spectrum analysis. These examples sufficiently demonstrate the divisibility of matter to be enormous, and whether this proceeds still further in colloidal solutions, so that even smaller particles may be present with the larger, which are detected by the ultramicroscope, is at present beyond our powers of observation.

IV. The Dispersoids and their Classification.

1. General Classification.

In consideration of the fact that suspensions, colloidal solutions, and proper solutions are comprehended as divisions of varying disperse grades, all three kinds of system are denoted (after P. P. von Weimarn)* by the common name dispersoids (*vide* p. 5).

The classification of the dispersoids will next be considered according to the grade of division or dispersion, and with Wo. Ostwald we distinguish :—

1. Proper or coarse suspensions ; among these are included suspensions and emulsions.

2. Colloidal solutions.

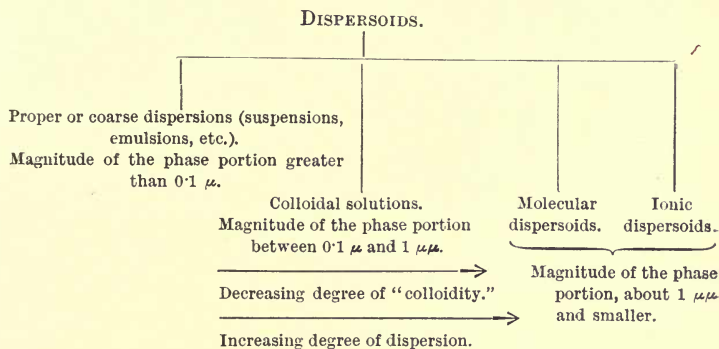
* With P. P. von Weimarn, compare *Koll. - Zeitschr.*, iii., 26 (1908).

3. Molecular dispersoids.

4. Ionic dispersoids (The Svedberg), assuming the existence of free ions. The term "ionic disperse system" has the same meaning.

3 and 4 correspond approximately to Graham's idea of crystalloidal solutions.

The dispersoids named are collected together in the following scheme (after Wo. Ostwald) :—



Emphasis must, nevertheless, be laid on the fact that between the separate groups of dispersoids transitions are conceivable, and these have actually been discovered by H. Picton and S. E. Linder. From a practical standpoint, however, the above classification is entirely suitable.

Colloidal solutions are further differentiated as suspension colloids and emulsion colloids ; for both

groups the shorter terms suspensoids and emulsoids are used (Wo. Ostwald, P. P. v. Weimarn).

2. Suspension and Emulsion Colloids.

A. SUSPENSION COLLOIDS.

From the term suspension colloids (suspensoids) are understood colloidal solutions having a solid disperse phase. As the term implies, they show analogy to suspensions; their characteristic representatives are the metallic hydrosols. As essential criteria of colloidal suspensions, the following may be cited :—*

1. The possibility of bringing about coagulation by centrifugal means. The precipitate is similar in properties to a fine solid powder.

2. The viscosity varies very little from that of the pure dispersion medium.

3. The optical heterogeneity is detected macroscopically as turbidity and opalescence; illuminated particles are to be seen in the ultramicroscope.

4. The Brownian movement. The velocity increases with rising temperature and decreasing viscosity of the dispersion medium. It should be noted that viscosity and temperature are dependent

* Compare Wo. Ostwald, *Grundriss der Kolloid Chemie*. (Dresden, 1909.) S. 100 ff.

on each other, inasmuch as rising temperature is usually accompanied by decreasing viscosity.

5. The existence of a distinct electric charge capable of detection. On the addition of electrolytes coagulations take place which are irreversible.

B. EMULSION COLLOIDS.

Emulsion colloids are colloidal solutions having a liquid disperse phase. They exhibit (as in the case of suspension colloids) analogies to the emulsions. Gelatine solutions afford examples of this type. Characteristic features are :—

1. The large internal friction (viscosity) ; even a small concentration essentially increases the viscosity of the dispersion medium. The rise in viscosity takes place with enormous rapidity as the concentration becomes greater. With rise of temperature the value of the internal friction sinks appreciably, in a gelatine solution, for example, whose temperature rises from 21° to 31° the viscosity diminishes about 1,000 per cent.

2. The ability to form foam.

3. Fluorescence—*e.g.*, emulsoids exhibit (as in general suspensoids also) colours diffusing by transmitted from reflected light.

4. Ultramicroscopically there is only a general illumination of the field of view to notice. Shining

particles are seldom present. With increasing dilution the brightness of the particles decreases.

5. The absence of electrical phenomena. Cataphoresis is at the most only feebly observed.

6. Coagulation only takes place by the addition of salt solutions of great concentration. The products of coagulation are very similar to liquids.

7. Ability to gelatinise and swell.

V. Preparation of Colloidal Solutions.

Since the time of Graham a number of investigators have made known to us the mode of preparation and the properties of many new colloids, and, during recent years especially, our knowledge of this new class of bodies has been enormously extended. The successful preparation of many crystalloidal substance in a colloidal state has also been accomplished, and thereby the distinction between crystalloidal and colloidal substances has been completely lost from Graham's standpoint; the ancient barrier fixed between them had to fall. We do not at the present time speak of a difference between colloidal and crystalloidal matter, but only separate the colloidal from the crystalloidal state of the body.

The chemistry of the colloids is the science of the colloidal state of matter.

The assumption has been put forward that when certain technical difficulties have been overcome by suitable experimental conditions, it will be possible to obtain all matter in the colloidal and crystalloidal states, so that both conditions may be regarded as normal states of matter. The following survey, which, however, has no pretensions to be complete, of bodies whose preparation in both forms has been accomplished, is now given.

1. A Summary of Matter known in the Colloidal and the Crystalloidal States.*

A. *Bodies known in both Colloidal and Crystalloidal States.*

I. INORGANIC SUBSTANCES—

1. ELEMENTS—

(a) Metalloids : carbon (?), phosphorus, sulphur, selenium, silicon, boron.

(b) *Metallic elements.*

(a) Light metals—Potassium, sodium, lithium, rubidium, caesium ;

Barium, strontium, calcium ;

Magnesium, lanthanum, aluminium, zirconium.

* Compare P. Rohland, *Koll.-Zeitschr.*, ii., 53 ff (1907).

(β) Heavy metals—Thorium, titanium, tantalum, niobium, tungsten, molybdenum, vanadium, chromium, uranium, manganese, cerium, arsenic, antimony, bismuth, thallium ;

Zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, mercury, silver, gold, platinum, palladium, iridium, osmium.

2. SULPHIDES.—The sulphides of selenium, tellurium, tungsten, uranium-molybdenum ; Arsenic, antimony, bismuth ;

Zinc, cadmium, tin, lead, iron, cobalt, nickel, copper, iridium, mercury, silver, gold, palladium.

3. OXIDES and HYDROXIDES.—Phosphoric acid, silicic acid, arsenic acid, barium oxide, vanadium pentoxide ;

Oxides of manganese, bismuth, iron, cobalt, nickel, copper, and mercury.

4. SALTS.—Sodium chloride, sodium carbonate, lead chloride, mercurous chloride ;

Barium sulphate, barium phosphate, barium chromate, barium carbonate.

II. ORGANIC COMPOUNDS—

The alkali salts of palmitic, stearic, cerotic, and oleic acids ;

Potassium iron tartrate ;
 Arabic acid, caramel, glycogen, the albumen
 of a hen's egg ;
 Benzopurpurine, benzdine dyes ;
 Indigo.

B. Substances known in the Colloidal State only.

I. INORGANIC SUBSTANCES—

1. HYDROXIDES.—The hydroxides of magnesium,
 lanthanum, yttrium ;
 Beryllium, aluminium, zirconium ;
 Thorium, titanium, tungsten, molybdenum,
 chromium, manganese, cerium, didymium,
 erbium ;
 Bismuth, tin, lead, iron, copper ;
 Gold.

2. SALTS AND OTHER COMPOUNDS.—Molybdenum
 blue, tungsten blue, molybdenum-tungsten
 purple, gold purple, Berlin blue, copper
 ferrocyanide, chromosulphuric acid (?).

II. ORGANIC BODIES—

Varieties of starch, dextrine, inulin ;
 Tragacanth, gum arabic ;
 Tannins, gallotannic acid ;
 The chyle of caoutchouc plants, caoutchouc,
 catechu, gambier ;
 Resins ;

Glue (gluten), gelatine, isinglass, agar-agar ;
The majority of albuminoids, the protoplasm
of cells.

2. Methods for the Preparation of Colloidal Solutions.

Only a cursory glance can be given to the numerous methods in use for the preparation of colloidal solutions ; for this purpose the known methods are divided into groups, of which only the first (comprising the chemical methods) will be explained intimately by examples.

A. CHEMICAL METHODS.

Under this heading will be grouped all those modes of preparation in which the sol may be obtained by chemical reactions in solutions through hydrolysis or reduction. This section follows approximately the temporal evolution of colloidal chemistry, and deals with certain sols in particular.

Hydroxides.

We may conveniently commence with this group, since the first bodies classed as hydrosols belong to it. These are silicic acid and the hydroxides of the iron group of metals.

1. SILICIC ACID.

In the year 1853 Kühn discovered a soluble silicic acid. This he obtained by stirring together a 3 per cent. solution of water glass and an HCl solution of density 1.1, the excess of acid being partly neutralised by a further addition of water glass solution, of which just so much was added as not to produce opalescence in the liquid. By warming to 25° , coagulation to a jelly took place, and this was washed with pure water by means of a cotton filter. The precipitate so treated was dissolved after 12 to 16 hours' boiling in pure water, forming a pseudo-solution, and leaving only a small residue. This pseudo-solution was then boiled down to a content of 6 per cent. silicic acid without the hydrogel being thereby precipitated. In transmitted light this hydrosol appeared perfectly clear; by reflected light, on the other hand, milk-white with a yellowish-red fluorescence; the silicic acid is precipitated as a jelly (*i.e.*, hydrogel formation) on the addition of sulphuric acid or by freezing, and this does not again dissolve in pure water.

Graham in the year 1861 obtained the hydrosol of silicic acid by pouring a solution of water-glass into dilute acid; he purified it by dialysis. The

silicic acid hydrosol so obtained gives with transmitted as well as with reflected light a perfectly transparent liquid, which by boiling may be considerably concentrated; on standing some days, however, the hydrogel separates out. The longer it is dialysed and the less contaminated by electrolytes, the more stable it will be. The pure hydrosol has a feeble acid reaction, in fact 100 grammes of the silicic acid contained therein neutralises 1.85 grammes KOH. Graham was of opinion that the neutral liquid so arising contained the hydrosol of a silicate, which he named a collisilicate. This hydrosol is more durable than that of the free acid, the latter, however, being more stable to small additions of hydrochloric acid. Minute quantities of carbonates rapidly bring about the separation of the gelatinous hydrogel of silicic acid, in contrast to the negative effect of acids or other salts; this property sharply distinguishes Graham's hydrosol from Kühn's, since the latter is transformed into the hydrogel, as above mentioned, on the addition of H_2SO_4 . Graham's hydrosol with a solution of glue gives a flocculent gel containing glue and silicic acid; in like manner casein also produces a gel. The behaviour, therefore, is exactly like that of tannic acid, which is also regarded as a colloid.

An extremely interesting, and at the same time simple, process was described by E. Grimaux in the year 1884. On saponification of a small quantity (8 gr.) of the methyl ester of silicic acid with much water (200 c.c.) and subsequent distillation of the methyl alcohol formed, a perfectly pure silicic acid hydrosol arises which is distinguished from that of Graham only by an even greater stability, and by the fact that carbonic acid does not produce gelatinisation either in the cold or hot.

2. FERRIC HYDROXIDE.

L. Péan de Saint-Gilles in the year 1855 prepared an iron oxide hydrosol as follows :—When a solution of ferric acetate is subjected to prolonged boiling, the original brownish-red colour changes gradually into brick-red, and its taste, which originally was astringently metallic, gives place to that of pure acetic acid. From this it follows that hydrolysis has taken place with the splitting up of ferric acetate into acetic acid and ferric hydroxide. The hydrosol so arising may be isolated from the acetic acid by prolonged heating at the boiling point, accompanied by the addition of steam, and appears in transmitted light to possess a perfectly clear deep brown colour, with deep brownish-red opalescence in reflected light. A trace of sulphuric acid

or of an alkali salt immediately generates the hydrogel, the precipitate so arising being insoluble in cold concentrated acids. Conversely if the hydrosol is poured into hydrochloric or nitric acid, there forms a granular, brick-red precipitate which, with pure water, is again converted into the hydrosol. F. W. Kreche in 1871 obtained the hydrosol of ferric hydrate by heating solutions containing less than 1 per cent. FeCl_3 , so causing hydrolysis to take place. If pure ferric chloride be added drop by drop to 1-2 litres of boiling water, a deep brown liquid immediately arises which exhibits every reaction of the ferric hydroxide hydrosol. The addition of strong acids causes hydrogel formation.

In the year 1890 E. A. Schneider described an interesting formation of the ferric hydroxide hydrosol; he discovered that AlCl_3 solutions are able to absorb a little freshly precipitated and washed ferric hydrate, which indeed on analogy with the solubility of ferric hydrate in ferric chloride solution is not remarkable. It is worthy of note, however, that the ferric hydrate remaining undissolved gives a dark brown hydrosol in pure water, after the salts also present have been removed as far as possible by filtering and washing the precipitate with a little water. The hydrosol is perfectly clear in transmitted light, but turbid and fluorescent by

reflected light. A drop of H_2SO_4 produces instant separation of the hydrogel.

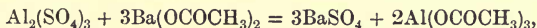
E. Grimaux obtains the hydrosol by a process analogous to that given for silicic acid—namely, by the saponification of the ferric ethylates.

3. ALUMINIUM HYDROXIDE.

The first to prepare the hydrosol was W. Crum (1854). He obtained by a suitable process a basic aluminium acetate soluble in water $\left[\text{Al} \begin{array}{c} \text{OH} \\ (\text{OCOCH}_3)_2 \end{array} \right]$.

This was accomplished as follows :—

He obtained by double decomposition, according to the equation :—



a neutral aluminium acetate, whose dilute solution placed in thin layers on glass plates at 38° gave the dibasic aluminium acetate. If a well-diluted solution of this be heated in a closed flask on the water-bath, after a prolonged interval, hydrolysis into free acetic acid and the hydrosol of aluminium hydrate takes place. The acetic acid is expelled from this hydrosol by boiling, accompanied by the addition of water ; no change is produced if the proportions do not exceed 1 part of alumina to 400 parts liquid. Addition of acids, except acetic, causes the hydrogel

to form, and this does not dissolve in excess of acid. The sulphates react in the same way, but the alkali salts of the above acids only cause precipitation when present in great excess, and the precipitates, when placed in pure water, pass again into pseudo-solution.

Graham prepared the hydrosol by dissolving freshly precipitated and well-washed alumina hydrates in AlCl_3 solution, and then submitting the liquid to dialysis. This hydrosol separates its hydrogel on dialysis, just as an iron hydrate hydrosol prepared by him does, before all the chlorine has passed into the water. It is very unstable; acids, alkalies, and salts all causing hydrogel formation; this instability sharply distinguishes it from that of Crum. The gel formed easily dissolves in an excess of the precipitating acid.

4. CHROMIUM HYDROXIDE.

Graham obtained the hydrosol by dissolving pure chromium hydroxide in a solution of chromium chloride and dialysing the liquid. It is coloured deep green, and behaves towards electrolytes like alumina hydrosol, except that it is somewhat more stable.

5. TITANIUM HYDROXIDE.

The hydrosol of titanitic acid arises, when titanitic acid, precipitated from its salts by ammonia, is dissolved in a little cold dilute hydrochloric acid, and this solution dialysed for several days; the hydrochloric acid thereby dialysing into the water, and the hydrosol of titanitic acid remaining behind in the dialyser. The preparation of the hydrosol is only successful if this at the most contains 1 per cent. titanitic acid, for otherwise spontaneous separation of the hydrogel takes place. (Graham, 1864.)

6. THORIUM HYDROXIDE.

Pure thorium oxide, obtained by heating thorium oxalate to redness, is warmed on the water-bath with concentrated nitric acid (whereby no external change is observed in the oxide), and then treated with water. A milk-white liquid arises, which possesses all the properties of an hydrosol. (P. T. Cleve, 1874.)

7. TUNGSTIC ACID (Graham, 1864).

This remarkable stable hydrosol is obtained in the following manner:—A 5 per cent. sodium tungstate solution is added to just the required

amount of dilute hydrochloric acid for union with the sodium, and the liquid then dialysed. After three days, pure tungstic acid hydrosol remains behind in the dialyser. The stability of this is so considerable that no acid or salt causes hydrogel transformation, while it may even be evaporated to dryness and heated to 200° without losing its ability to form a pseudo-solution with water. The transformation only takes place on heating to redness. Graham prepared from the dry residue liquid hydrosols of widely varying content—viz., of 5, 20, 50, and 80 per cent. tungstic acid. All these hydrosols evolve carbonic acid with Na_2CO_3 , and form a true sodium tungstate solution from which the salt, undergoing transformation, separates crystalline.

8. MOLYBDIC ACID.

The hydrosol corresponding to the above has been prepared by Graham in an identical manner to that for tungstic acid by the decomposition of the sodium salt with excess of hydrochloric acid. It has a yellow colour, and presents similar properties to the tungstic acid hydrosol. According to A. Lottermoser, it is even as stable as the latter body.

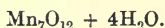
9. STANNIC ACID.

The hydrosol is prepared according to Graham by dialysing tin chloride which has just been decomposed by alkali, or by decomposing a sodium stannate solution with hydrochloric acid. In the dialyser it first forms a jelly, but with the removal of the salts this gradually changes into the hydrosol. The hydrosol of metastannic acid arises on heating the stannic acid hydrosol. Both hydrosols are transformed into hydrogels by minute quantities of electrolytes. R. Zsigmondy prepared (1898) the hydrosol in the following way:—By prolonged passing of air through a stannous chloride solution containing about 0.15 gramme tin per litre, and kept clear by a small excess of hydrochloric acid, there arises in four to five days by simultaneous oxidation and hydrolysis a gelatinous stannic acid. This by decantation and washing on the filter may be completely freed from salts, and when moistened with a little ammonia passes over in pure water into a perfectly clear hydrosol when viewed both in reflected and transmitted light. A largely diluted stannous chloride solution likewise undergoes hydrolysis on standing, forming a gelatinous stannic acid hydrogel, which in the manner above described may be converted into the hydrosol. The two gels

under consideration exhibit some differences in behaviour; the first is soluble only in dilute, the second in concentrated hydrochloric acid and caustic potash solutions. Zsigmondy is of opinion that this may be an intermediate stage between ortho and metastannic acids, or perhaps a mixture of both.

10. MANGANESE HYDRATE.

W. Spring and G. de Boeck made (1887) the observation that when a neutral potassium permanganate solution is treated with a reducing agent a brown precipitate containing potassium arises, which, however, has no fixed composition. After several decantations with water a dark brown hydrosol forms. It may not be filtered, since the paper fibre causes gel formation, while electrolytes separate the hydrogel. An analysis of the residue after diluting the liquid gave the formula—



Sulphides.

In addition to the colloids named, almost all the sulphides of the heavy metals, which earlier had only been known as insoluble precipitates, have been transformed into hydrosols. Hans Schulze, in the year 1882, was the first to describe the preparation of arsenic and antimony sulphides.

1. ARSENIC AND ANTIMONY TRISULPHIDES.

When sulphuretted hydrogen is conducted through a neutral aqueous solution of arsenic trioxide no precipitate forms, but the liquid gives by transmitted light a reddish-yellow colour, on much dilution a yellow colour, and with reflected light exhibits a deep yellowish-red fluorescence. The hydrosol of arsenic trisulphide has, therefore, been formed. Only on the surface of the liquid does a thin skin of the hydrogel arise, and this may be easily removed by filtration without altering the hydrosol. In like manner its stability is unimpaired when heated to boiling, although hydrolysis of the sulphide gradually takes place, yielding sulphuretted hydrogen and the corresponding amount of arsenic trioxide. By dialysis of the entire liquid the oxide diffuses, leaving the pure hydrosol. The behaviour towards electrolytes further establishes the colloidal character of the arsenic sulphide. Almost every electrolyte, with the exception of very weak organic acids, causes gel formation. After expelling the water, insoluble arsenic trisulphide remains behind.

With this hydrosol H. Schulze first discovered the law according to which different electrolytes promote gel formation. He placed together 10 c.c. of the salt to be investigated, and 2 to 3 drops of

the arsenic sulphide hydrosol, then observed whether gel formation took place or not. By the regular alteration of the degree of dilution of the electrolytes Schulze has been able to determine the limits to the gel forming capacity of different electrolytes. It was established that strong acids produced gel formation in much more dilute solutions than weak, while many organic acids had no effect whatever. Salts act in proportion to the valency of the metal contained therein—*i.e.*, salts of trivalent metals produce the gel with a relatively less concentration of their solutions than the divalent, and these in turn with less than monovalent metals, in order to bring about the same effect. In the case of double salts the gel formation is according to the metal of highest valency. In addition, the acid part of the salt exerts an influence on gel formation, this being in the following order :—Chloride, sulphate, nitrate.

The hydrosol of antimony trisulphide was prepared by H. Schulze in the same way as that of arsenic.

2. FERROUS AND COPPER SULPHIDES.

These were obtained in the colloidal state by L. T. Wright (1883) ; the pure hydrosols, however, have not been prepared.

3. COPPER SULPHIDE.

In the year 1887 W. Spring and G. de Boeck made a communication on the above in their work, entitled *Sur le sulfure de cuivre à l'état Colloidal*. Copper sulphide precipitated from a neutral or ammoniacal solution of a copper salt changes after many decantations with sulphuretted hydrogen water into an hydrosol. When concentrated it is perfectly black, when dilute brown and clearly transparent, but has a greenish fluorescence in reflected light. It is stable only if at the most 5 grammes CuS are contained per litre, while every electrolyte transforms it into the hydrogel. The same law for gel formation by electrolytes holds good for copper sulphide as in the case of arsenic sulphide mentioned earlier.

4. CADMIUM SULPHIDE (E. Prost, 1887).

Cadmium sulphide is precipitated from an ammoniacal cadmium sulphate solution, washed with pure water, then suspended in water and H_2S passed through the liquid. The original flocculent sulphide gradually distributes itself after the manner of milk throughout the liquid, and finally disappears, leaving a homogeneous solution. H_2S , therefore, exerts here a peptisating effect on the hydrogel of cadmium sulphide. The excess of H_2S may be

completely expelled on prolonged boiling of the hydrosol, without any change taking place, and, moreover, no gel formation is caused by the paper fibre on filtration. The hydrosol has a beautiful golden yellow colour, is perfectly transparent, and somewhat fluorescent by reflected light. On prolonged standing the gel separates out, the latter behaviour being accelerated by weather liable to thunderstorms. In this respect cadmium sulphide hydrosol resembles milk, the latter also containing an hydrosol. Among those electrolytes which cause gel formation of cadmium sulphide hydrosol, the cadmium salts have by far the greatest energy of precipitation.

5. OTHER SULPHIDES.

Mercuric sulphide hydrosol was prepared by C. Winssinger in the year 1888 after the method given for the hydrosol of copper sulphide. In concentration it is deep black and opaque, diluted it is brown with a greenish fluorescence. The same author has also prepared the sulphide hydrosols of W, Mo, Pt, Au, Pd, Ag, Th, Pb, Bi, Fe, Ni, and Co., by obtaining the respective sulphides in very dilute solution, and removing the salts present by dialysis. Zn and In sulphide hydrosols were obtained by a method depending on the formation

of the sulphide in a liquid, where the reaction conditions are such that no electrolyte except water is generated.

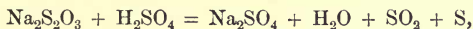
Finally, E. A. Schneider obtains tin sulphide hydrosol by treating stannic acid hydrosol with H_2S ; after heating an intense yellow colouration appeared, an indication that the oxide hydrosol had been transformed into the sulphide hydrosol. A drop of hydrochloric acid brings about immediate separation of the tin sulphide hydrogel.

Elements.

1. SULPHUR.

Sulphur may be obtained in many varieties of colloidal state. M. Raffo * produces it easily and in large quantities in the following manner:—Concentrated solutions of sodium thiosulphate are allowed to fall drop by drop into cold concentrated sulphuric acid ($D = 1.84$).

According to the equation—



there arises a sulphur hydrosol, which in a few hours becomes turbid, owing to the separation of amorphous sulphur. This amorphous sulphur changes with time into the crystalline variety.

* See *Koll.-Zeitschr.*, ii., 358 ff (1908).

2. SELENIUM.

The selenium hydrosol is obtained, according to H. Schulze (1885), by reducing selenic acid (SeO_2) with a 7 to 8 per cent. solution of sulphur dioxide, and cooling. The acid is neutralised by an addition of ammonia and the excess of this neutralised with oxalic acid. The liquid is then centrifuged, whereby the colloidal selenium is separated from the dispersion medium. The precipitate is dissolved in water forming the colloidal solution. The latter is coagulated by KCl , K_2SO_4 , and Na_2CO_3 , not, however, by acetic, tartaric, or oxalic acids, or ammonia. The density of colloidal selenium is 4.26 according to Cholodny.* From the agreement of this number with the density of amorphous selenium, the author concludes that amorphous selenium may be present in the colloidal solution.

3. GOLD AND GOLD PURPLE.

The first to investigate colloidal gold was J. B. Richter, the discoverer of chemical equivalent weights; his researches, however, remained for a long time unknown.

In 1857, M. Faraday noticed that a dilute solution of gold chloride was gradually reduced by yellow

* *Journ. d. russ. phys. Chem. Ges.*, xxxviii., 129 (1906).

phosphorus in such a way that a ruby red liquid was formed which in general changes quickly, depositing gold, but may often remain for long periods unchanged. Additions of electrolytes instantaneously effects this transformation, causing a colour change to violet and a precipitation of finely divided gold. Faraday was attracted by the striking resemblance of the colour of this gold liquid to that of gold ruby glass, and optical examination confirmed this similarity. Later, other investigators have obtained red gold solutions by employing different means of reduction.

R. Zsigmondy, for example, has proposed the following reduction process :—25 c.c. of a solution containing 0.6 gramme of gold chloride hydrochloride per litre were diluted with 100 to 160 c.c. water, 2 to 4 c.c. of N solution of potassium carbonate or bicarbonate added, and the whole heated to boiling. As soon as ebullition commences the flame is removed and 4 c.c. of a solution containing 1 part of freshly distilled formaldehyde in 100 parts water are added drop by drop, but fairly rapidly and with vigorous stirring. Colloidal gold solutions prepared according to these directions may be kept for months. They may be concentrated until the gold content is 0.1 per cent., and purified by dialysis. Such concentrated hydrosols gradually deposit gold.

Electrolytes all act with energy, causing a sudden colour change from violet to blue, and precipitating black gold. The electric current separates a black powder at the anode. That the hydrosol contains gold and not an oxide has been proved by Zsigmondy, who heated to redness the substance obtained by precipitating the hydrosol with common salt, but was unable to find oxygen present even by a spectroscopical test.

According to A. Gutbier, colloidal gold may be obtained as follows:—1 gramme gold chloride is dissolved in 1 litre of the purest distilled water, and neutralised with a little strongly diluted sodium carbonate solution. To the above a very dilute cold solution of hydrazine hydrate (1 : 4,000) is added. Immediately on the addition of the first few drops reduction takes place with the formation of a deep dark blue colour, and after a few c.c. have been added the reduction is complete. The colour is almost indigo blue, and the sols may be kept after dialysis. By filtration through a paper filter no change takes place, but addition of electrolytes on the contrary brings about decolouration. The red hydrosol may also be obtained by the addition of hydroxylamine hydrochloride. By the use of very dilute solutions of hypophosphorous acid as an addition to the neutral gold chloride, and care-

fully pouring in distilled water, the solution appears a clear green. With phenylhydrazine hydrochloride A. Gutbier produced, by suitably concentrating this solution, the red, violet, and, finally, the blue gold sol.

Purple of Cassius.

An especial interest has been centred for a long time in the purple of Cassius, which is formed by the reduction of a diluted gold solution with stannous chloride. Using partially oxidised stannous chloride there arises not a red but an indigo blue precipitate. Two hypotheses have been put forward as to the nature of gold purple. The gelatinous purple-red precipitate which when pure appears homogeneous, was regarded by J. J. Berzelius on the ground of its homogeneity and solubility in water as a chemical compound of stannic acid with gold and tin oxides. The other view is that the gold may be present as metal. Schneider has solved the problem by a synthesis of gold purple. He found that the solubility of gold purple in ammonia was due to its colloidal nature—*i.e.*, ammonia peptises the hydrogel to hydrosol. The ammonia may be completely removed on dialysis. Schneider's method of synthesis was as follows:—He treated an alloy of gold, tin, and silver with concentrated nitric acid,

whereby it is split up into a black powder. After careful washing it was taken up with ammonia, thereby giving a ruby-red colour. By the addition of electrolytes the hydrogel is formed, and this may be boiled down on the water-bath to a jelly capable of being again taken up by water, and exhibiting a ruby-red colour. The hydrosol is decolourised by potassium cyanide, whereby stannic acid separates. Great excess of hydrochloric acid merely produces a sudden colour change to violet. On dialysing this solution finely divided gold remains on the membrane, since the tin can diffuse through the partition as chloride. The view that the purple is due to stannic acid and metallic gold receives substantial support from the fact that Schneider succeeded in obtaining the gold purple by the reduction of gold with oxalic acid in the presence of stannic acid hydrosol. Yet from the beginning Zsigmondy regarded it as settled that gold purple hydrogel was an intimate mixture of colloidal gold and colloidal stannic acid. This decision is, therefore, important as showing how easily one may be deceived with regard to chemical compounds, and also because it may be of value in many other cases. Actually towards electrolytes the gold behaves in this colloidal compound, not as colloidal gold, but as if "it were attached to the molecule of stannic

acid." To establish its colloidal nature, Zsigmondy, like Schneider, employs dialysis. Zsigmondy refined his process so well that he succeeded in producing dark red to rose colours with hydrosols richer or poorer in gold content, and by the use of a violet or blue gold hydrosol he obtained even violet or blue varieties of purple. The absorption spectra of the purple hydrosols are identical with those of gold hydrosols, the colour, therefore, depending only on the gold, since stannic acid hydrosol is colourless. On the other hand, the stannic acid hydrosol obscures the properties of gold hydrosol. We know that from a pure gold hydrosol electrolytes precipitate insoluble gold after a sudden colour change to dark blue. If, however, the gel be separated from the purple hydrosol by electrolytes, no sudden colour change is observed, and the precipitate formed is coloured a beautiful red. The gelatinised purple may be again transformed into the hydrosol with a little ammonia, while the coloured pure gold does not exhibit these properties. In a sentence, the unstable gold hydrosol is rendered more stable by the presence of stannic acid, and assumes the properties of this stable hydrosol. It follows, then, that mixed colloids possess properties not possessed by any separate colloid, but derived partly from the one, partly from the other.

A perfect analogy to the behaviour of purple of Cassius is shown in the following experiment :—If common salt be added to gold hydrosol, coagulation takes place, accompanied by a sudden colour change to blue. A small addition of gelatine, gum, or albumen prevents this colour change, and protects the gold against the precipitating action of electrolytes. It has been shown that such protective action is exerted by reversible colloids on irreversible. If the mixture of both colloids be evaporated, then a dry residue soluble in water is obtained, analogous to gold purple of Cassius.

4. THE PLATINUM METALS.

Platinum hydrosol was observed by C. Winkler in the year 1885, when, after reducing platinum from its salts by means of sodium formate, the reduced platinum passed through the filter paper on washing, and formed a black opaque liquid. A. Lottermoser obtained platinum hydrosol as a brownish-black liquid which gradually deposits metallic platinum, by a similar method to that proposed by Zsigmondy for the preparation of gold hydrosol. By previous dilution and subsequent dialysis a stable hydrosol was obtained. Lottermoser prepared in like manner the hydrosols of

palladium, rhodium, and iridium ; the two latter, however, are unstable.

5. SILVER.

Silver hydrosol was first definitely discovered, and thoroughly investigated within recent times, by the American, Carey Lea * ; it had been known as such, however, for a long time, but had been regarded as the hydrosol of a salt of silver suboxide. Already, in the year 1839, F. Wöhler had observed that on heating horn silver at 100° in a stream of hydrogen, the original white salt darkens by degrees, and will dissolve in much water, showing a brownish-yellow colour ; the acid reacting solution separates a metallic silver mirror after a short interval. Wöhler regarded the brown solution as containing a salt of silver suboxide. By a similar process with silver citrate he obtained a wine-red solution, which on heating turns green and rapidly precipitates metallic silver. A precipitate, thought by Wöhler to be silver suboxide, is produced in the red liquid by caustic potash solution. HCl forms a substance concerning the nature of which Wöhler did not pronounce. At the present time we know the red liquid to contain silver hydrosol, which is

* Compare Carey Lea, *Kolloides Silver u. die Photohaloide* (Dresden, 1908).

precipitated by electrolytes, such as KOH and HCl, being naturally, however, mixed with oxides and chlorides respectively, since it contains dissolved besides the hydrosol some oxide salt of silver (W. Muthmann, 1887). By the very gradual addition of electrolytes there commences a colour transformation from red through yellow to green before precipitation takes place. On treating the reduction product with a little ammonia, a grass green liquid was immediately obtained, from which electrolytes also separate metallic silver. By dialysis the colouring matter remains behind, a proof of its colloidal nature. The purified hydrosol is much more stable than the impure, and for its precipitation larger quantities of electrolytes are requisite. Animal charcoal abstracts the colouring matter from all these hydrosols. The behaviour towards gum arabic is interesting. If the red liquid be mixed with a gum solution, then if the gum be precipitated by alcohol, the red substance is carried down with it. By dissolving again in water the latter also goes into solution. The analysis of the substance precipitated from the red liquid gave 98·91 per cent. of Ag—i.e., almost pure silver—from which it undoubtedly follows that the red liquid contains silver hydrosol. In the year 1889 Lea prepared colloidal silver in the following way :—

200 c.c. of a 10 per cent. silver nitrate solution was added in the cold to a mixture of 200 c.c. of a 30 per cent. ferrous sulphate solution, and 250 c.c. of a 40 per cent. solution of sodium citrate, which had been rendered alkaline. In this way a bluish coloured precipitate ensues, which settles very slowly, and by decantation of the supernatant liquid can finally be freed by filtration from the reduction liquid, thereby assuming a steel blue colour. It is transformed by water into a deep bluish-red opaque hydrosol, which, however, is still contaminated with iron salts and citric acid; these may be almost completely removed by repeatedly taking up the solid hydrosol with water and reprecipitating with ammonium nitrate until iron can no longer be detected. The hydrosol then assumes a brownish-red to coffee-brown colour. On washing with 95 per cent. alcohol the hydrosol passes into the gel in which Lea found 97 per cent. silver, the rest being citric acid and iron.

That the preparation is at this stage pure silver was proved by Lea, who heated the specimen he analysed to a high temperature, whereby neither H nor O, and at the most only a little CO_2 , was obtained. The citric acid, however, is not present in definite atomic relationship to the silver, a fact known from the varying amounts of the same;

also it is in no way united to the silver, since after washing the substance with water, and evaporating, until all the colloidal silver had been transformed into the grey metal, no trace of citric acid could be detected. The colloidal nature of the red liquid was established by dialysis. The hydrosol allows the silver to be precipitated by almost every substance, even by gum arabic. Acids bring about the precipitation of ordinary grey silver from both the hydrosol and the gel. The purple-brown hydrogel may be transformed into the hydrosol by various salts—*e.g.*, potassium sulphate.

Employing potassium sodium ferrotartrate for the reduction of silver nitrate solution, and using these reagents in very dilute condition, neither silver hydrosol arises nor even ordinary grey silver, but a preparation which exhibits under certain conditions a beautiful golden lustre. The red precipitate formed at the beginning darkens by degrees, and on drying assumes a most wonderful golden lustre when dusted in thin layers on glass or paper; if it be subjected to prolonged washing, then a coppery lustre is obtained. Lea is of opinion that an allotropic modification of silver is present in all cases where, on the reduction of silver solutions, a red or brown colour appears. The liquids so produced, however, are very unstable.

A. J. A. Prange, in the year 1890, arrived at practically the same results as Lea, only he succeeded in making still purer silver preparations. The most concentrated sol prepared by Prange contains 4.75 grammes silver per litre ; it is syrupy, possesses a colour like bromine, and rapidly deposits a black precipitate. E. A. Schneider materially improving on these methods, obtains an hydrosol containing 12.248 grammes of silver per litre. He also succeeded in transforming this hydrosol into an organosol—viz., into an ethylalcosol, and into a glycerosol. The alcosol appears chlorophyll green with a bluish cast in transmitted light, and a light brownish-violet by reflected light. After dialysing for twelve days Schneider obtained a beautiful wine-red organosol. Ether precipitates colloidal silver from the alcosol. This solid sol (*vide* p. 15) may be dried without passing into the gel. The silver mirror remaining on the glass has a complementary colour to that of the sol.

For medical purposes colloidal silver is now technically prepared by a process similar to that of Lea.

Every electrolyte causes gel formation in the hydrosol, with the exception of the chlorides of the heavy metals, which are reduced to —ous chlorides with the formation of silver chloride,

together with a little silver. Recently A. Gutbier has proposed a very interesting process for the preparation of colloidal silver, which is analogous to that for the gold sols described above (*vide* p. 54). Solutions of hydrazine hydrate (1 : 2,000), hydroxylamine hydrochloride, and hypophosphorous acid serve as reducing agents.

6. MERCURY.

A. Lottermoser obtains the hydrosol from mercurous nitrate by reduction with stannous chloride, avoiding a large excess of acid. It is coloured deep brown, while the addition of acids or salts causes precipitation. The tin chloride arising during the reduction transforms the colloidal mercury partly into mercurous chloride, whereby gel-formation ensues. Stannous nitrate is a much more suitable reducing agent. The reduction takes place in a very dilute solution of mercurous nitrate, whereby a deep brown, opaque liquid arises.

7. BISMUTH AND COPPER.

The hydrosol of bismuth is obtained when ammoniacal solutions of bismuth salts are reduced by stannous chloride. The solutions employed must be diluted.

Copper hydrosol is obtained as follows :—After the preparation of an alkaline cupric salt solution by means of sodium citrate, an alkaline solution of stannous chloride is carefully added, the whole being heated on the water-bath. At first a milky turbidity forms in the solution, which turns yellow, then red, and finally black. The fine black precipitate forms a reddish-brown hydrosol with water. That the latter contains metallic copper is well observed by the ready oxidation of the metal, for the surface of the hydrosol quickly assumes a greenish colour through union with atmospheric oxygen, in time, however, changing to yellow. Tartaric acid and caustic soda solution are more preferable than sodium citrate.

C. Paal's Process for the Preparation of Colloidal Solutions.

C. Paal and his colleagues succeeded in preparing colloidal solutions of gold and silver, by warming the sodium salts of lysalbinic and protalbinic acids (*i.e.*, the decomposition products of egg albumen and casein, obtained by treating albuminous matter with alkalies), with silver nitrate and gold chloride respectively, and adding caustic soda solution. The albuminous bye-products serve as reducing agents, so that elementary silver and gold are

respectively formed. The metals, however, do not separate as precipitates, but remain in solution as colloids, since the albuminous derivatives act as protective colloids. On repeated precipitation from the silver and gold sols, by means of acids, and re-dissolving in alkalies, the preparation becomes richer in colloid, and may be purified from the other substances present by dialysis. C. Paal obtained preparations containing 90 per cent. and more of silver. For the preparation of colloidal solutions of different substances a special reducing agent other than either of the sodium salts of lysalbinic or protalbinic acids must be employed. The following are suitable as such:—Hydrazine, hydroxylamine, sodium amalgam, aluminium, and hydrogen. To obtain colloidal platinum, palladium, copper, tellurium, and selenium, hydrazine hydrate (or hydroxylamine hydrochloride) are employed. Of the reducing agents enumerated sodium amalgam serves best for colloidal iridium, aluminium for colloidal osmium; the latter may also be obtained by treatment with hydrazine hydrate, and a subsequent reduction with gaseous hydrogen at 30° to 40° . Colloidal copper may be prepared by the action of hydrogen gas on the solid hydrosol of copper oxide. According to the properties of the solutions a red or blue hydrosol is

obtained from copper, a brown or blue from tellurium. The special advantage of this method lies in the fact that the hydrosols of many metals are obtained in greater concentration and more solid form.

B. ELECTRICAL METHODS.

In addition to all the former comprehensive methods * which have been employed for the preparation of colloidal solutions, there still remain for consideration two interesting modes of obtaining sols which depend on the pulverisation of compact metals by means of the electric current.

The Methods due to G. Bredig.

That metals were pulverised into extremely fine, cloud-like particles when a powerful electric discharge passed between them had been known since the time of J. W. Ritter and H. Davy. When this fine dust was caught on glass plates, it was possible to prepare extremely thin layers of the finest metallic powder. For employing this method in the preparation of colloidal solutions science is

* An exhaustive collection of all the known methods for preparing colloidal solutions of inorganic substances is contained in the comprehensive work—*The Svedberg*, “Die Methoden zur Darstellung kolloider Lösungen anorganischer Stoffe.” (Dresden, 1909.)

indebted to G. Bredig (1898). This investigator discovered, while experimenting on the decomposing action of the electric arc on different liquids, that metals are so disrupted and scattered as to form dark liquids if an arc is established under pure water between wires composed of these metals.

The details of the experiment were originally as follows :—A direct current arc was established between rods or wires of the metal to be pulverised under water contained in a well-cooled basin made of Jena glass or porcelain. The strength of the current was between 5 and 10 amperes, the E.M.F. between 30 and 110 volts. Gold wires, 1 mm. thick and 6.8 cm. long, are suitable for the preparation of gold hydrosol, these being brought in contact, and after starting the current are separated 1 to 2 mm. apart, thus establishing a small electric arc. During the gentle hissing of the arc, gold is shot out from the cathode in blue or dark purple red clouds, and is distributed partly as sol and partly as a coarse suspension. The latter is obtained especially with 5 to 7 amperes, while a current strength of 10 to 12 amperes causes a finer and more uniform disruption, furnishing a dark bluish-red sol. The pulverisation of the metal takes place much more efficiently if a trace of caustic soda solution be added to the water. This pro-

cedure furnishes deep red gold hydrosols, only a little coarse gold remaining behind on filtration. After some weeks or months the colour of the gold, according to the mode of preparation, changes to a bluish-violet; with more careful preparation it may be kept for periods ranging from several months to two years. Bredig proved that the cathode was the chief participant in the disruption. Gold sols contain about 14 mg. gold per 100 c.c.

The preparation of platinosols is quite analogous, except, however, that an addition of alkali is superfluous. Platinum wires 2 mm. thick are suitable with a current strength of 5 to 6 amperes. The most concentrated sols contain 20 mg. platinum per 100 c.c. of solution.

In a similar way Bredig prepared the sols of palladium and iridium, while the silver sol was obtained with the greatest ease.

The Svedberg Method.

Bredig's process, with many modifications, and brought to greater perfection, has been worked by The Svedberg since 1905.

The metal which has to be converted into the sol by pulverisation was suspended as foil in the dispersion medium; into the vessel containing the liquid dip two electrodes made of metals, such as

aluminium and iron, which offer great resistance to pulverisation. A very feeble current was employed, the current strength being 20 to 50 milliamperes. When a condenser is inserted the disruption proceeds very quietly ; in this way Svedberg succeeded in preparing colloidal tin and also colloidal gold, silver, copper, and lead in different solvents. The method was still further improved by the use of inductors, several condensers, and a Wehnelt interruptor. The discharge was oscillatory. Under these changed experimental conditions, colloidal zinc, cadmium, and lead were prepared. With still further improvements (viz., by the use of a large inductor and a mercury interruptor designed by Boas) uniform oscillatory discharges were made possible. By means of a direct current arc using a very small current strength it was not possible to acquire complete colloidal subdivision ; on the other hand, very interesting results for comparison are obtained by this method.

The degree of subdivision is most intimately dependent on the spark length, since the shorter the spark the more complete the state of division. Using this method, Svedberg could obtain, under suitable experimental conditions, all the alkali metals in the colloidal state. For the latter ethyl ether proves a most suitable dispersion medium.

The sols are obtained as exquisitely coloured liquids by this wonderful disrupting and scattering process. Svedberg made profound investigation into colour regularities, the following being worthy of note, viz. :—That the colour of the metal was the same in both colloidal and gaseous states.

The Swedish investigator was also able to obtain the alkaline earth and most other metals in colloidal condition, these, however, being of varying stability. The isobutylalcosol of mercury can only be retained one to two hours ; on the other hand, that of bismuth and many other metals for an unlimited time.

Of the non-metals, carbon, silicon, selenium, and tellurium were obtained in the colloidal state by this process. Minerals also, such as magnetite, copper glance, and molybdenum glance admit of easy disruption.

These sols exhibit the Tyndall effect, and, therefore, prove themselves to be heterogeneous.

VI. Research Methods. Ultramicroscopy.

In this section the methods of research in use for colloids are more thoroughly described, since only after careful observation and correct experimental interpretation is it permissible to propound theories on the nature of the colloidal state, and

such a course will afford greater satisfaction than theoretical explanations, if attempted.

We have known since the time of Graham that inability to diffuse is generally due to colloidal character, and, therefore, to osmotic pressure. If this is not always the case, and in colloids, for example, it is extremely small, but at the same time definitely present, there are good reasons for the assertion made in the introduction that the idea of "colloid" is not capable of exact definition. Meanwhile only typical colloids will be considered, and of these there is an overwhelming number, so that we are able to accept the inability to diffuse as a colloidal characteristic. The relative experimental investigation has been mentioned in the introduction, and, therefore, may be passed over in this place, especially as it was simple in the highest degree. By the above we acquire an opinion as to the nature of the substances to be investigated. If, then, the problem is to establish the identity of an hydrosol prepared by a new method with the hydrosol of an earlier investigator, an exact macroscopical examination is first made. This includes the natural colour, the colour by reflected and transmitted light, and the existence of fluorescence, the latter property, as noticed in the previous section, being characteristic of many hydrosols. Spectroscopic analysis

also renders good service, since the ability to absorb certain rays of white light is one of the fundamental properties of every substance. Further, the mode of formation of a newly prepared hydrosol has to be compared with those of earlier discovered sols, and from this to find out if a deviating method is capable of giving the same result; the earlier known methods of investigation frequently afford such information. The stability of the hydrosol must also be tested at higher temperatures, and the behaviour of the sol under these conditions carefully noted. Finally, the effect of electrolytes must be studied, since alteration by electrolytes is a permanent characteristic of sols. Should no change be recorded, then the presence of protective colloids must be sought for. By proceeding as above, we shall gain a more definite comprehension of the hydrosol, and may readily establish its identity with one already known. If several properties be identical, while others are not, then we may conclude with greater probability that the hydrosol is impure, and postpone our decision until further purification, followed by a repetition of the investigation, has been made. If the properties of a reliably pure hydrosol be known, then much valuable information may be gained about the impure hydrosol.

From a scientific standpoint the further question, how to gain by a comparison with known data—*e.g.*, from crystalloidal solutions—an insight into the nature of the colloidal state is of interest. At the present time this question has received a satisfactory solution since the ultramicroscope has opened out a new channel for researches into the nature of colloids.

The development of the ultramicroscope begins with the observations of Fizeau and H. Ambronn, according to whom very narrow slits of light are still visible, even though their breadth falls much below the limits of microscopical resolving power. The narrower the slit of light, the less, naturally, is the brightness of its microscopical image. R. Zsigmondy, by the aid of these facts, was able to establish with certainty the existence of coarse particles in gold hydrosols. He examined two strongly turbid hydrosols by means of a converging beam of light (sunlight) with a hundredfold magnification, and was able to detect the presence of thousands of glittering gold particles, whose size, he estimated, as being less than the wave-length of light. By ordinary illumination they could not be perceived with the best objectives. Another experimental arrangement was, therefore, adopted; sunbeams entering from the roof of the room were

horizontally reflected by a mirror and concentrated with a lens, whose focus was feebly magnified by the microscope. The glass, containing the liquid for investigation, stood on the object table of the microscope, in such a position that the focus of the lens lay in the middle of the liquid.

In the year 1900 Zsigmondy investigated solutions of glue, gelatine, stannic acid, etc., and, in addition, to the general illumination of the cone of light, he was able to perceive separate particles. With silver hydrosol, however, he saw a dazzling bright cone of light, which was only resolved into separate particles when the solution was extremely dilute. An almost clear gold solution (containing only 0.005 per cent. Au) gave a green cone of light, which disappeared on dilution without separate particles having been detected. Another similarly diluted gold solution allowed in general only solitary gilded dust particles to be recognised. That gold was still present was proved by coagulation with common salt, whereby the liquid appeared densely filled with active glittering particles. It was therefore established that gold in different grades of division may be contained in a liquid, without these settling, and it has been shown that apparently gold may be divided as far as optical heterogeneity. Zsig-

mondy was able, by means of microscopic magnification, to ascertain approximately the known gold content, and the mean distance and average mass of the separate particles.

A far-reaching improvement for making visible the ultramicroscopic particles was due to H. Siedentopf. In this the essential innovations were the introduction of the bilateral slit and the use of microscopic objectives with the illuminating arrangement. From Siedentopf, also, originates the theory connected with the method of rendering visible ultramicroscopic particles, as well as calculation of the probable limits to their perceptibility.

The reason why, in the earlier microscopical methods of investigation, separate particles were not observed is obvious. They were generally examined by transmitted light, and since the eye was dazzled by the quantity of light which enters it, small differences in brightness due to diffraction of light by the very small particles were imperceptible, for the same reason that small differences in brightness are not detected in daylight. In order to render the smallest particles visible, these must be subjected to as intense illumination as possible, no illuminating ray must meet the eye directly, and an extremely dark background is necessary. The

details of the ultramicroscope * are of great interest, but principles only can be given here. Some expressions, however, need explanation. A particle is said to be ultramicroscopic which lies beyond the resolving power of the microscope (in practice about $\frac{1}{4} \mu$); according as the ultramicroscopic particles may be visible or not, they are termed submicroscopic or amicroscopic. After what has been previously recorded, the terms ultra-, sub-, and a-microns, as used by Zsigmondy, should be obvious.

The microscopical image of the cone of light in a colloidal solution is approximately as follows:—The distances between the particles are usually smaller than $\frac{1}{4} \mu$; in this case the converging beam appears more or less intense, homogeneous, and is polarised; often larger isolated particles are present, which scintillate, causing the cone of light to appear heterogeneous. In order to decide the nature of solution, extreme dilutions must almost always be taken (from 0.001 to 0.0001 per cent. or even further); eventually the spaces will be great enough to admit of microscopic resolution. If the diffracted light from the separate particles is

* Respecting this subject, the reader may be referred to Zsigmondy, *Zur Erkenntnis der Kolloide* (Jena, 1905); and A. Cotton and H. Monton, *Les Ultramicroscopes et les objets ultramicroscopiques*. (Paris, 1906.)

of sufficient intensity to form an impression of light on the retina of the eye, then microscopical images of the particles will be perceived as diffraction patches. With submicrons under favourable illumination this is always the case. Should the diffracted light be too feeble, then the cone of light gradually disappears with increasing dilution, nothing more may be recognised, the solution becomes optically empty, and contains amicrons. In this case the presence of extremely finely divided matter is capable of easy proof by the addition of a precipitating agent, which is itself optically empty. By such means the dissolved colloidal particles unite to form greater, and these frequently densely fill the field of vision (*e.g.*, gold, albumen). As already mentioned, the transmitted light, after passing through the hydrosol to be investigated, is polarised, often indeed when the particles have become so great after coagulation that they may be recognised by the naked eye.

The investigation into the size of the particles leads only to an average value. It is made in the following manner:—If A be the contained mass of the distributed material per unit volume, and n the number of particles in the same space, then $\frac{A}{n}$ is the average particle mass. A suitable and definite

illuminated volume has to be chosen, its magnitude determined, and the number of particles therein counted. The mass A of the distributed substance, therefore, follows without further calculation from the concentration. Since, however, the particles are in continual motion, it is impossible to ascertain a large number by counting. The illuminated liquid volume must, therefore, be so restricted, or the solution so diluted, that about 2 to 5 particles on the average, a number readily established at a glance, are seen in the field of vision. The smallest particles which under the best of circumstances may be made visible amount to $5\mu\mu$. The cubical dimensions of the particles, which may be ascertained by merely considering the specific gravity of the solid body, are obtained from the formula $l = \sqrt{\frac{A}{Sn}}$ (where S stands for the specific gravity). If the particles are amicroscopic, then a cone of light can scarcely be perceived, and sometimes not at all, but the particles are regarded as amicroscopic if but the tint of the cone of light be recognised. Should the particles on sufficient dilution be just perceptible in the brightest sunlight, then we have the smallest submicrons (about $6\mu\mu$). If the particles are still larger ($15\mu\mu$), they may just be detected in the light of the electric arc. Particles

of magnitude 22 to 38 $\mu\mu$ are always bright and gleaming in varying tints ; their mobility decreases with increasing magnitude. Particles larger than 75 $\mu\mu$ sink to the bottom ; they must, however, be about 250 $\mu\mu$, in order to be observed in the microscope by ordinary illumination.

The appearance of the motion of such ultramicroscopic particles, which lie near the limit of visibility in sunlight, is surprisingly brilliant. The motion is uncommonly active, similar to a swarm of dancing midges in sunlight ; the particles frisk, dance and leap, approach and retreat. This movement is the expression of continual admixture of the liquid, and lasts for years with retainable liquids. The particles hurry through the field of view in zig-zag directions almost with the speed of lightning (Zsigmondy). A representation of this ultramicroscopic motion true to nature has been accomplished by cinematograph,* but can only be perceived by special intuition.

VII. Recent Views on the Nature of the Colloidal State.

1. The Solution Theory.

From the preceding (*vide* pp. 4 and 74) we know that colloidal solutions are not homogeneous,

* Compare v. Henri, *Kinematogr. Studie kolloider Lösungen. Compt. rend.*, clix., 1024-1026 (1908).

therefore even at the outset a solution theory has little prospect of effectual success. Yet it is worthy of close consideration, since in its development much that is of interest has been evolved, although it seems to give no valid reason for every case of gel formation, and if the sols be regarded as true solutions, then gel formation receives an explanation which is not free from objection. An osmotic pressure, by whose aid the molecular weight of the dissolved body may be determined in true solutions by an application of the laws of Raoult and Van't Hoff, has actually been observed by W. Pfeffer (1877) in a gum solution ; J. H. Gladstone and W. Hibbert have also indirectly proved the presence of osmotic pressure by the freezing and boiling point methods ; these investigators, in like manner, have found the molecular weights of gum, caramel, and ferric hydroxide. N. Ljubavin determined the lowering of the freezing point due to colloidal silicic acid. These results agree unusually well with the molecular weights ascertained from theory ; A. Sabanejew and N. Alexandrow found the molecular weight 14,700 from the lowering of the freezing point of an albumen solution. C. E. Linebarger found the molecular weight of dextrine to be 1,083, corresponding to $(C_6H_{10}O_5)_7$. From these and numerous other experiments it follows that, in general,

the application of Raoult's law to colloids shows the latter to possess extraordinarily large molecular weights. This property is characteristic of colloids, and Sabanejew distinguished inferior colloids having a molecular weight less than 30,000 (tungstic and molybdic acids) from superior—the typical—which show no measureable lowering of the freezing point, and, therefore, possess an extraordinarily high molecular weight (starch, silicic acid, ferric hydr-oxide, silver). Soluble colloidal substances have, therefore, exceptionally large molecules, which may be imagined as arising from the agglomeration of smaller molecules. The assumption of large molecules also explains the inability of the majority of colloids to pass through animal membranes, since their molecular complexes are too great for penetration of the partition pores. In certain hydrosols (such as those of the metallic hydroxides, but not of metals) gel formation may be represented as a meeting of the already large molecular complexes present forming still larger microscopic aggregates, which become visible, accompanied by water separation (this obviously being impossible in the case of metallic sols). Linebarger regards these colloidal solutions as true solutions in which an osmotic pressure has actually been observed. A true characteristic of solution is exhibited according to

Ch. Lüdeking and E. Wiedemann by an observed heat of solution. This is in agreement with the fact that A. J. A. Prange found an evolution of heat when gel formation takes place in the silver hydrosol.

Also, Zsigmondy, who in earlier years had been an adherent of the solution theory (*vide* p. 21), regarded the gold contained in his gold hydrosol as being really dissolved, since he could never detect an increase in brightness of the upper liquid layer such as would be present on the eventual subsistence of the gold particles. I believe that we can only accept this solution theory at the present time tentatively, since we are scarcely in a position to accept sols as being homogeneous in the light of these results which ultramicroscopic investigation has afforded, for in a true solution homogeneity is proved even with the most delicate instruments of research. (As a true solution, one thinks, for example, of a common salt or copper sulphate solution.)

2. The Adsorption Theory.

If gelatinous silicic acid be placed in fuchsine solution, the dye cannot be removed even by most thorough washing—in scientific phraseology it has been adsorbed by the jelly. Similar phenomena

were found by Linder and Picton with other colloids, for example, on coagulating arsenic trisulphide hydrosol by means of barium chloride solution a part of the barium is precipitated with it (the corresponding amount of chlorine passing into solution). Albuminous matters also take up dyes and salts when coagulated. In addition to colloids, wood charcoal, and in general all other porous bodies, on account of their surface tension, possess an adsorption ability which is naturally only a physical process. Since then colloids exhibit adsorptive tendencies, and, as above mentioned, mainly the precipitated gels, we must assume from what precedes that the gels have undergone great surface development. How this comes about, and how it must be regarded, I will now attempt to explain.

If (according to J. Traube) a drop of 2 per cent. solution of potassium ferrocyanide be added to a 3 per cent. copper acetate solution, then by avoiding any shaking, a thin, coherent membrane—"precipitated membrane"—of copper ferrocyanide is formed, and this under strong magnification shows a granular structure. A whole series of similar precipitate forms are known—*e.g.*, "Myelin forms"—which arise on mixing cholesterine and soap water, are fibrous. O. Bütschli obtained very

similar forms during his investigations on foam formation. By shaking xylol, for example, with soft soap he obtained an insoluble substance, which separated as a coherent membrane and formed a honey-combed meshwork of almost macroscopic structure. A similar scum arises on shaking oil with water containing a little potassium carbonate ; when the water is evaporated, the oil brightens, but retains enclosed the dissolved potassium carbonate. On moistening the scum is again formed.

Here we find an analogy to the behaviour of gels during sol formation. J. M. van Bemmelen, indeed, regards gels as precipitated membranes, which form a meshwork of amorphous coherent parts, these being swollen with enclosed liquid, and on treatment with water pass, under the circumstances, into the hydrosols. Van Bemmelen found that by removing the water from colloidal hydroxides, different chemical compounds holding varying amounts of water are not formed by stages, but that the water content of these hydrates changes continuously. They give up the requisite amount of water in order to equalise the vapour pressure of the gel with its surroundings. The vapour pressure curve has no discontinuities. The investigator named regards colloidal as adsorption compounds of changing water content. The coagulation of an

hydrosol brings about a separation, whereby a tissue of colloidal substance forms, which is a transition between the solid and liquid states, the tissues enclosing liquid. This structure is considered by Bütschli as being in general honey-combed; the separate cells are 1 to 5 μ , and have been observed by him in gelatine, glue, albumen, starch, and silicic acid. The structure makes possible the replacement of the enclosed water (Imbibitionswasser) by other liquids, and also explains the permeability of the gels. On heating, the gels part with their adsorption ability, whereby van Bemmelen supposes a contraction of the cells to take place. To the enormous surface development with the honey-comb formation, and, therefore, to the enormous surface tension involved, are traced the peculiarities of the colloidal state.

Hydrosols form structures in which the separation of solid molecular complexes from the solvent begins, a fact proved by the heterogeneity of hydrosols, opalescence, visibility of the smallest particles, and minute osmotic pressure.

By the aid of this theory a series of properties of colloidal solutions can be explained. The sols are not ordinary solutions, but contain a phase of molecular complexity distributed throughout the dispersion medium. This explains the essential

deviations from crystalloidal solutions—*e.g.*, the absence of an osmotic pressure, lack of diffusion ability, and electrical conductivity. Elevation of temperature in many cases causes separation, in which the dispersion medium is parted from the colloid, which then forms a persistent, narrow-meshed texture (*e.g.*, the coagulation by heat of albuminous bodies). The drying up of gels is a continuous occurrence, in which the dispersion medium is eliminated with decreasing velocity. The process of drying furnishes a very narrow-meshed product, which, however, frequently possess the ability to absorb again the dispersion medium, and so pass over into the swollen state.

The adsorption theory explains that additional fact that separating gels seize upon electrolytes or isolated ions, this action being due to the great surface tension of colloids.

We have also, while judging this theory in conjunction with the preceding one, acquired the important evidence afforded by the ultramicroscope, which allows us to accept the adsorption theory with greater satisfaction. I believe, however, that, while this theory contains something which throws light on colloidal nature, yet the final decision can only be made when further progress has been made in researches into the colloidal state. To me,

especially, the best explanation is obtained by a union of this adsorption theory with the suspension theory to be described next ; later, I will discuss the two theories together (*vide* p. 92).

3. The Suspension Theory.

M. Faraday conducted experiments with his colloidal gold solution (*vide* p. 52) to investigate the condition of the gold. By means of a lens he allowed a concentrated beam of sunlight to pass into the liquid, whereby he perceived clearly the presence of a turbidity. He regarded the latter as a proof of the existence of suspended gold. Later, H. Schulze expressed the view that the gels of arsenic and antimony trisulphides exhibit a behaviour to their sols similar to the different modifications of sulphur and phosphorus, and he assumed smaller molecular complexes for the sols than for the gels.

Most investigators now hold the view that in the hydrosol no true solution of the colloid is present, but only a suspension of very small particles. This assumption receives powerful support from a method by which many hydrosols may be prepared. In this way L. T. Wright obtains iron sulphide hydrosol by treatment of the gel with potassium cyanide in insufficient amount to cause complete solution,

while E. A. Schneider produces ferric hydroxide hydrosol by a partial solution of the gel and reception of the residue in water. This procedure may be represented as taking place in such a way that the larger molecular complexity of the gel is gradually reduced by detachments, until the necessary degree of minuteness has been attained, in order to remain permanently in pure water as a suspension, or to form an hydrosol. Accordingly, the fact that heat is evolved during gel formation from an hydrosol by means of electrolytes may be explained, for, in order to obtain so fine a division of matter, work must be done. The precipitation of hydrosols and coarse mechanical suspensions by means of electrolytes may be looked upon as analogous phenomena ; every small particle may be regarded as being surrounded by a water envelope corresponding to its sphere of activity. Should these spheres of activity intermingle, then the hydrosol or suspension remains stable, if on the contrary the spheres of activity are isolated, then gel formation or sedimentation of the suspension takes place respectively ; the problem restated, then, is whether the addition of electrolytes or elevation of temperature brings about contraction of these spheres of activity. Conversely with more minute division the particles have their spheres of activity intermingled, and the

gel passes over into the sol. This analogy between coarse mechanical suspensions and hydrosols had already (in the year 1883) been demonstrated by Ebell, who found that the deep blue apparently clear washing of ultramarine in water, often persisted for months, and even passed unchanged through filter paper; it was precipitated, however, by electrolytes in the manner of an hydrosol. When magnified 1,200 times by the microscope the washing appears as small points, and must, therefore, be regarded as a suspension.

J. W. Spring (in the year 1900) published detailed observations on gel formation from hydrosols and cluster formation in fine suspensions; he distinguishes two kinds of colloidal solution—viz., that which, when dried in vacuo, exhibit a matted, sinuous fracture of the triturated residue, and that possessing a vitreous residue, which is lustrous and extraordinarily firm. The latter he considers as an easily liquefiable jelly, which on dilution contracts more and more until finally a varnish-like pellicle remains; the former he regards as consisting of more independent particles. Naturally between these two classes are also intermediate forms. Spring, Schulze, and Winssinger found, in addition, that the precipitating ability of salts depended on the kation, and that those with the highest valency

operate with the greatest energy. By employing solutions of equal conductivity, every electrolyte with the same kation causes the same velocity of precipitation, independent of the anion.

The assumption that hydrosols are a suspended colloidal condition obtains further support from experiments made by Linder and Picton; these investigators have attempted to filter many kinds of hydrosol through porous clay under pressure. Only certain very dilute arsenic sulphide and also silicic and molybdic acid hydrosols admit of filtration through porous clay, while all the remaining colloids are held back from their hydrosols, the filtrate containing no trace of the same. The suspended particles are, therefore, too large to penetrate the filter pores. The inability of colloids to pass through animal membranes receives now an obvious explanation. Other arsenic sulphide hydrosols behave like the rest of the colloids in having no diffusion ability; in addition, many hydrosols, as Graham had already observed, diffuse with great difficulty, and, therefore, we have confidence in stating (as already intimated on p. 22) that there exists a gradual transition from suspensions to true solutions. How remarkably the evidence from optical methods supports the assumption of a suspension state in colloidal hydrosols has been appreci-

ated in Chapter vi. Hydrosols, then, are regarded as suspensions of extremely finely divided matter. According to Wilhelm Ostwald, matter in this state possess properties other than those in the ordinary condition. According to A. Coehn, the behaviour of these hydrosols, which exhibit a small osmotic pressure in contrast to coarse mechanical suspensions which never do so, affords support to the above explanation. On account of this behaviour G. Tammann concludes that the colloids possess a high molecular weight.

The Raoult methods for the determination of the freezing point depression and the boiling point elevation due to colloids may, therefore, be employed to ascertain their molecular weights. E. Paterno found the molecular weight of gallic acid corresponded to the formula $(C_7H_6O_5)_{109}$, while a similar high molecular weight was found for tannin; in glacial acetic acid, however, both substances exhibit the normal (the simplest) molecular weight. This is a proof that the colloidal state of many bodies only exists in certain dispersion media (in the above case water), while in other solvents the substances behave as crystalloids. From these facts Paterno derives the hypothesis for the nature of hydrosols, that the latter contain colloidal substances which are swollen to a certain degree, and that these are present

as complicated molecular complexes, which are only disintegrated by particular solvents. Inorganic hydrosols, so far as they are stable at high temperatures (as, for example, a stannic acid hydrosol investigated by A. Lottermoser), show no elevation of the freezing point in pure water. In like manner S. E. Linder and H. Picton could establish no depression of the freezing point for the hydrosol of mercuric sulphide. We must assume, therefore, that the Raoult law is not valid for colloids, or that the molecular weight of the colloid present in the hydrosol approaches an infinite value—*i.e.*, the same as in the swollen state, or in a homogeneously distributed suspension. This swelling may be regarded as adsorption, and this without abandoning the suspension theory, for the particles when endeavouring to form spheres of activity attain this by an adsorption of liquid, since the spheres of activity intermingle to form, as it were, a continuous whole (p. 89).

Finally, the behaviour of hydrosols with respect to the electric current may be mentioned. According to C. Barus and E. A. Schneider, the silver hydrosol, as also the gel, are almost perfect insulators. Colloidal silver, therefore, behaves like mercury vapour, which is also known not to conduct the electric current. Linder and Picton, however,

have shown a wandering of the particles to take place. Basic colloids, such as ferric hydrate, are repelled from the anode, while acids are attracted. This behaviour is analogous to the wandering of particles in mechanical suspensions, and must, therefore, be regarded as additional evidence for the suspension theory. However, in both cases traces of the particles have probably gone into solution, otherwise the behaviour towards the electric current might not be capable of explanation. This solution is perhaps bound up with a kind of ionisation, since the electro-chemical nature of the particles is supported by the fact that certain colloids are mutually precipitated, and under these circumstances electrolytes may be dispensed with. From what precedes the solution theory comes once more into prominence, and so the nature of the colloidal state does not appear to receive a complete explanation on any single theory, although from reasons already cited we must award the greatest preference to the suspension theory.

I cannot in this place enter more fully into the excessive number of theories put forward to explain the properties of colloidal solutions, but will only urge that the majority of these seek to explain the relations of colloidal solutions on the ground of their particular properties. From the description

of the colloids in Chapter v. (*vide* p. 32 *et seq.*), it is a common characteristic that electrolytes have the power of producing coagulation. The ability to precipitate depends on the valency of the kation (*vide* p. 17). The disperse phase wanders when the electric current is applied, and other properties clearly point to the fact that the sol particles are electrically charged, a view already stated on p. 13. Adherents of the suspension theory, which by the ultramicroscope has received the most palpable proof, now seek to explain these electrical and electro-chemical properties by additional theories. It must here suffice to state the names of those investigators who have worked to perfect the suspension theory. They are—W. B. Hardy, G. Bredig, H. Freundlich, J. Billitzer, and G. Quincke. For more complete information on the above and other theories the excellent work of A. Müller, *Allgemeine Chemie der Kolloide* (Leipzig, 1907), may be referred to. I will now content myself with describing somewhat fully the

Crystalline Theory of P. P. von Weimarn,*

on account of the great interest it evokes. This theory is a special form of the suspension theory which deals more completely with the form of the

* Compare *Koll.-Zeitschr.*, ii., 81 (1907), and numerous works in other volumes.

disperse phase. The ultramicroscope only informs us as to the appearance of the particles in colloidal solutions, not, however, on the more exact relations and the conditions of the separate particles. The theory of P. P. von Weimarn states that the particles of colloidal solutions are crystalline. The more complete generalisation drawn by the author named is that the crystalline state is the only possibility of matter. Accordingly gases, liquids, and solids are crystalline. For gases and liquids evidence of crystallinity does not exist, so that only the question of the crystalline nature of solids need detain us. P. P. von Weimarn puts forward the following data in support of the assumption that the disperse phase is crystalline :—

For the formation of a precipitate solutions having a definite concentration must be employed. During the course of several experiments it was found that certain concentrations caused precipitates to incline towards the crystalline state, while with greater or less concentrations the reacting liquids formed crystals always less distinctly, until finally these could not be identified even under the microscope. With certain solution concentrations, then, crystal formation may be observed ; at lower concentrations than those tending to crystal formation, the magnitude of the crystals continuously

decreases with increasing dilution, until finally what we term colloidal solutions arise ; it is, therefore, probable that the smallest particles—viz., the ultra- and a-microns—possess a crystalline character.

The disperse phase of suspensoids has, in addition, the ability to bring about the supersaturation of molecular disperse solutions ; a- and sub-microns in contact with their dispersion medium have the ability to stiffen into microcrystalline structures.

Finally, many optical properties support the assumption of a crystalline disperse phase (*e.g.*, the scattering of colour in the ultramicroscopic image).

VIII. The Importance of Colloidal Chemistry to other Sciences.

COLLOIDAL CHEMISTRY AND MINERALOGY.

The importance of colloidal chemistry for mineralogy was first recognised by F. Cornu, and this only recently.* Cornu called attention to the fact that a large number of natural minerals exhibit the appearance and properties of gels. To this class belong the minerals designated porodin by Breithaupt.

Cornu found, for example, that the oxidation zones

* See the special number of the *Koll. Zeitschr.* for May, 1909. "Kolloidchemie und Mineralogie."

of ore beds contain many colloidal bodies (chrysocolla, stilpnosiderite, copper pitchblende), and after further investigation he obtained evidence that the gels are far more distributed in nature than had hitherto been supposed. The author named found gels in the following mineral groups :—

Hydroxides.—Bauxite, stilpnosiderite, opal, psilomelane, wad.

Hydrated Phosphates.—Delvauxite, diadochite, variscite, evansite, fischerite, lead uraninite.

Hydrated Arsenates.—Pitticite, ganomalite, lavendulane.

Hydrated Antimonates.—Bleinière, thrombolite, antimony ochre in part.

Hydrated Silicates.—Chrysocolla, gymnite, plombierite.

The gels of aluminous silicates—*i.e.*, the normal weathered products of silicates, or the bodies formed in the oxidation zones of ore beds.

Elements.—Anthracite, sulphur (as a swollen deposit), probably also certain varieties of pure gold and silver.

Sulphides.—Argentite (Ag_2S), amorphous greenockite (CdS), black amorphous mercuric sulphide, covellite (CuS), metastibnite.

Haloid Salts.—Ostwaldite (Cornu), horn silver

corresponding to the well-known precipitate of silver chloride.

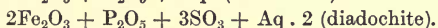
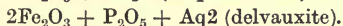
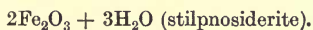
The general results of Cornu's investigations are as follows :—

1. The gels of the mineral kingdom are the typical products of every normal weathering process.

2. To every crystalloidal mineral there corresponds in nature a similarly composed gel (Law of Homoisochemite).

3. The gels of the mineral kingdom have stalactitic, botryoidal, and glassy forms, fibrous fractures, with a soapy or earthy feel, now and then being found in a gelatinous condition.

4. By adsorption there arise complex bodies from more simple—*e.g.*, the following series :—



Colloidal chemistry teaches mineralogy to understand the origin of dendrites, those tree-like branched structures which R. F. Liesegang was able to obtain by diffusing a molecular disperse solution into a gel. H. Leitmeier was able to prove that natural dendrites and the artificial precipitate forms of Liesegang are quite analogous formations. Solutions could, so far as surface formations were not developed, penetrate into the crevices of solid

masses, and so furnish dendrites by sedimentation or coagulation. Many dendrites also arise by diffusion.

Further, mineralogy is indebted to colloidal chemistry for the explanation of colour in crystals. Siedentopf has established that the colour of blue rock salt is due to finely divided sodium. Minerals coloured by colloidal particles have their colour changed by radium emanation. Such an emanation may, on the other hand, induce colour which disappears on heating. The colours of colloidal substances must be carefully distinguished from the above, since they are due to the presence of isomorphous substances—*e.g.*, the ruby is tinted by isomorphous chromium oxide mixed with it.

COLLOIDAL CHEMISTRY AND AGRICULTURE.

That colloidal chemistry is called upon to solve a series of extraordinarily important questions in applied science is clear, when the fact is considered that the most essential components of plant and animal life, starch, cellulose, and albumen, belong to the colloids.

Colloidal chemistry stands, therefore, in manifold relationship to agriculture, and van Bemmelen has rendered pioneer service by solving a series of closely connected problems. The soil is indebted

to its hydrogel content—viz., the hydroxides of aluminium, iron, and silicon—for its ability to adsorb the colouring matters, and the soluble colloidal substances oozing through the earth; a fact of greatest importance when manuring. In like manner valuable compounds are received by the plants, which otherwise would be carried away by water. Of the acids, colloidal humus substances chiefly adsorb phosphoric, but not hydrochloric, nitric, and sulphuric acids. Essentially stronger is the adsorption affinity for bases, which, however, is exerted in varying degree. The series—sodium salts, lime, and magnesia—are adsorbed more feebly than potash. The adsorption is, therefore, weakest for sodium salts and lime. Natural pastures, however, are already saturated with sodium salts and lime. A kind of substitution, therefore, takes place if such pastures are treated with potassium salts, in which the sodium and lime salts are exchanged for those of potassium, the former being therefore left behind. This is the reason why potassium is more indispensable for plant growth than the other less important and partly unnecessary bases.

According to P. Ehrenberg, with the exception of humus colloids, the plant mucus possesses properties similar to those of colloids, indeed the coarser



suspensions of clay, bacteria, and salt are of importance in the adsorption process. The condition of the soil, however, is not constant, since its physical properties change by the action of frost, heat, and moisture. Moreover, the addition of salts (in the form of dung), and the biological activity of the plants themselves, are of influence.

COLLOIDAL CHEMISTRY AND MEDICAL SCIENCE.

Colloidal chemistry has also acquired importance as a valuable scientific aid to medical science,* since almost every component of the organism consists of colloids or results from the same. Certain new therapeutic remedies have been discovered which owe their efficiency to the high degree of colloidal dispersion. Of these, the following may be mentioned :—Collargol (silverhydrosol), Hyrgol (mercury hydrosol), and Collaurine (gold hydrosol).

IX. The Importance of Colloidal Chemistry in Chemical Industry and Technology.

A large number of chemical industries use colloids without the importance of these colloidal substances being sufficiently appreciated. To-day we know that the peculiarities of colloidal nature have

* See special volume of the *Koll. Zeitschr.* for December, 1909, on "Kolloidchemie und Medizin."

received interesting application in Industry, for example, in the manufacture of starch, cellulose, celluloid, glue, leather, resin, caoutchouc, artificial silk, paper, photographic plates, and paper. Only a few facts of importance in technology can be described here, but the excellent brochure of K. Arndt, "Bedeutung der Kolloide für die Technik," Dresden, 1909, may be consulted for more complete details.

GLASS MANUFACTURE.—Many coloured glasses are tinted by colloidal metals. The beautiful red coloured golden ruby glass is obtained by an addition of gold chloride to the glass melt, from which particles of gold separate when the glassy mass becomes hard; these particles, however, have at first the magnitude of amicrons, so that the glass appears colourless. By heating anew until the glass becomes soft, the particles grow until they attain the size of ultramicrons, to which the cause of the red colour is to be traced. The preparation of copper ruby glass is performed by an analogous method.

For the manufacture of silver mirrors, a silversol prepared by a reduction process is used. The silver may be more uniformly distributed the purer the silver sol. The metal is placed on the glass as a continuous cover by bringing a very fine silver

stratum on the purified glass surface, this, like a germ, causing coagulation of the silver sol.

In the earthenware trade, colloids likewise play a part. In the natural state clay does not possess complete colloidal properties, but acquires these when stored. The purest clay—*i.e.*, kaolin or China clay—must be stored for months, winter and summer alike. Thereby the crystalline kaolin passes into the colloidal state, and is then plastic to the highest degree.

Bound up with the plasticity is also frequently an enhanced tenacity, such being peculiar to glutinous materials. For example, the adhering force of glue is due to its great plasticity, by virtue of which the glutinous matter penetrates into crevices and unites with every unevenness, forming a firm meshwork.

In the binding of cement, the mass arising from the calcium hydrosilicate gels and aluminates is regarded as changing into a crystalloid (according to an older explanation the solidity of cement depends on salt formation—*i.e.*, the union of silicic acid with calcium).*

In the manufacture of moist sugar, colloids play a part in the extraction of the moist sap. The

* Compare Wilh. Michaelis, sen., *Der Erhartungsprozeß der kalkhaltigen hydraulischen Bindemittel*. (Dresden, 1909.)

albuminous matters remain for the greater part in the beetroot cells, while the cell sap—*i.e.*, a sugar solution—diffuses into the surrounding liquid.

Lüppo-Cramer has employed colloidal chemistry with great success to solve photographic problems. In photography colloidal silver compounds are used, and their changes of state furnish varying adsorption compounds. The colloidal nature of gluten, and of glutinous wheat, makes possible its extraction as a coherent adhesive mass of extraordinary tenacity. The dressing of leather depends on the mutual behaviour of hide and tannin. The hide absorbs tannins, and so becomes leather. The dyeing industry also depends on the formation of similar adsorption compounds.

The caoutchouc industry has to deal intimately with a typical colloid in caoutchouc.

In sewage purification the impure colloids have been successfully retained as adsorption compounds. Upon an analogous behaviour depends the use of isinglass for the clarification of liquids.

The importance of colloidal chemistry is, therefore, extraordinarily manifold, and up to the present has not reached its highest development.

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INDEX.

A

ACETIC acid, Glacial, 8, 92.
 Adsorption theory, The, 83.
 Alcosol, 4, 63.
 Alexandrow, N., 81.
 Aluminium hydroxide, 41.
 Ambronns, H., 74.
 Animal charcoal, 60.
 Anion, 17.
 Arndt, K., 103.
 Arsenic and antimony trisulphides, 47.

B

BARUS, C., 93.
 Bemmelen, J. M. van, 85, 86, 100.
 Berthelot, 27.
 Berzelius, J. J., 55.
 Bilateral slit, 76.
 Billitzer, 95.
 Bismuth, 64.
 Boas, Mercury interruptor of, 70.
 Bodies known in both colloidal and crystalloidal states, 33.
 Boeck, G. de, 46, 49.
 Boiling point, Elevation of, 7.

Bredig, G., 5, 21, 23, 67, 68, 69, 95.
 Breithaupt, A., 97.
 Brown, R., 9.
 Brownian movement, The, 9, 10, 11, 14, 30.
 Bruyn, C. A. Lobry de, 23.
 Bunsen, R., 28.
 Bütschli, O., 84, 86.

C

CADMIUM sulphide, 49.
 Calcar, R. P. von, 23.
 Caoutchouc industry, The, 105.
 Cataphoresis, 13, 14, 32.
 Cement, Binding of, 104.
 Centrifugal force, Use of, 23, 30.
 Characteristics distinguishing colloid from crystalloid solutions, 23.
 Cholodny, 52.
 Chromium hydroxide, 42.
 Citric acid, 61.
 Clay, 104.
 Cleve, P. T., 43.
 Coagulation, 15, 32.
 „ point, 17.

Coehn, A., 92.
 Collisilicate, 38.
 Colloids, 2, 3, *et seq.*
 ,, Inferior, 82.
 ,, Superior, 82.
 Colloidal alkali metals, 70.
 ,, chemistry, and agricul-
 ture, 100.
 ,, chemistry, and medical
 science, 102.
 ,, chemistry, and mineral-
 ogy, 97.
 ,, solutions, Colour of, 13,
 18, 25, 57, 58, 61, 62.
 ,, solutions, Preparation
 of, 32.
 ,, solutions, Properties of,
 6.
 ,, solutions, Relation of, to
 solutions proper and
 suspensions, 20.
 ,, therapeutic remedies,
 102.
 Colour in crystals, 100.
 Copper, 64, 65.
 ,, Sulphide, 48, 49.
 Cornu, F., 97.
 ,, general results of in-
 vestigations, 99.
 Crum, W., 41, 42.
 Crystalline disperse phase, 97.
 ,, theory of P. P. von
 Weimarn, 95.

D

DAVY, H., 67.
 Dendrites, 100.

Density, 6.
 Dextrine, Molecular weight of,
 81.
 Dialysis, 2.
 Diffraction, 12, 76, 77, 78.
 Diffusion, 2, 8.
 Disperse heterogeneity, 5.
 ,, heterogeneous system, 5.
 ,, phase, 6.
 Dispersion medium, 6.
 Dispersoids, 5, 8, 28.
 ,, Classification of, 28.
 Dyeing industry, The, 105.

E

EARTHENWARE trade, 104.
 Ebell, W., 90.
 Ehrenberg, P., 101.
 Electric arc, 68.
 ,, charge, 13, 31.
 ,, conductivity, 14.
 ,, osmose, 14.
 Electrical and magnetic proper-
 ties, 13.
 ,, methods, 67.
 Electrolytes, 15, 16, 25, 54.
 ,, Precipitating capacity
 of, 17, 18, 31, 90.
 Elements, 33, 51, 98.
 Emulsion colloids, 30, 31.
 Eykmann, 8.

F

FARADAY, M., 21, 52, 53, 88.

Faraday-Tyndall cone of light, 21.
 Ferric hydroxide, 39.
 Ferrous sulphide, 48.
 Fizeau, 74.
 Flocculation, 15.
 Fluorescence, 31.
 Foam, Ability to form, 31.
 Freezing point, Depression of, 7.
 Freundlich, H., 95.

G

GALLIC acid, 8, 92.
 Gels, 5, 15.
 General characteristics, 1.
 Gladstone, J. H., 81.
 Glass manufacture, 103.
 Glycerols, 4, 63.
 Glue, 1.
 Gold, 7, 21, 25, 52.
 ,, purple, 52.
 ,, value, 18.
 Graham, Th., 1, 2, 4, 8, 15, 22, 32, 37, 38, 39, 42, 43, 44, 45, 72, 91.
 Grimaux, E., 39, 41.
 Gum arabic, 60.
 Gutbier, A., 54, 55, 64.

H

HALOID salts, 98.
 Hardy, W. B., 13, 15, 95.
 Hibbert, W., 81.
 Hofmann, A. W., 27.

Homoisochemite, Law of, 99.
 Hydrated antimonates, 98.
 ,, arsenates, 98.
 ,, phosphates, 98.
 ,, silicates, 98.
 Hydrosols, 4, 7, 12.
 ,, Reversible and irreversible, 15, 16.
 Hydroxides, 34, 35, 36, 98.

I

IMPORTANCE of colloidal chemistry to other sciences, The, 97.
 ,, of colloidal chemistry in chemical industry and technology, 102.
 ,, of potassium salts, 101.
 Inferior colloids, 82.
 Influence of acid part of salt on gel formation, 48.
 Inorganic substances, 33, 35.
 Ionic disperse system, 29.
 Ionisation, 94.
 Isinglass, Use of, 105.

J

JELLIES, Properties of the, 14, 19.

K

KAOLIN or China clay, 104.
 Kation, 17, 90.

Kinetic theory of gases, 27.
 Kirchhoff, 28.
 Konowalow, D., 21.
 Kreche, F. W., 40.
 Kühn, H., 37.

L

LAW governing mutual precipitation of colloidal solutions, 19.
 Lea, Carey, M., 59, 61, 62, 63.
 Leather, Dressing of, 105.
 Leitmeier, H., 99.
 Leplay, H., 8.
 Liesegang stratification figures, 20, 99.
 Linder, S. E., 21, 29, 84, 91, 93.
 Linebarger, C. E., 81, 82.
 Literature, 106.
 Ljubavin, N., 81.
 Lottermoser, A., 16, 44, 58, 64, 93.
 Lüdeking, Ch., 83.
 Lüppo-Cramer, 105.

M

MACROHETEROGENEOUS system, 5.
 Magnetic properties, 14.
 Manganese hydrate, 46.
 Manufacture of moist sugar, 104.
 „ of silver mirrors, 103.
 Manuring, 101.
 Mercury, 64.

Metals, Heavy, 34.
 Methods for the preparation of colloidal solutions—
 Chemical, 36.
 Electrical, 67.
 Meyer, W., 8.
 Microheterogeneous system, 5.
 Microns, Ultra-, Sub-, α -, 77, 97.
 Molybdic acid, 44.
 Müller, A., 95.
 Muthmann, W., 60.
 Myelin forms, 84.

N

NATURE of the colloidal state,
 Recent views on the, 80.
 Nernst, W., 20.
 Nomenclature, 1.

O

OPALESCENCE, 30.
 Optical properties, 12.
 Ore beds, Oxidation zones of, 98.
 Organic compounds, 34, 35.
 Organosols, 4, 63.
 Oscillatory discharge, 70.
 Osmose, 2.
 Osmotic pressure, 7, 72, 81.
 Ostwald, Wilh., 20, 92.
 Ostwald, Wo., 5, 28, 29, 30.
 Oxidation zones of ore beds, 98.
 Oxides, 34.

P

PAAL, C., process for the preparation of colloidal solutions, 65, 66.

Parchment paper, 28.

Paterno, E., 8, 92.

Péan de Saint-Gilles, 39.

Pectisation, 15.

Pfeffer, W., 81.

Photographic problems, 105.

Picton, H., 21, 29, 84, 91, 93.

Platinum metals, The, 58.

Porodin, 97.

Potassium sodium ferrotartrate, 62.

Prange, A. J. A., 63, 83.

Precipitation, 15, 90.

Prost, E., 49.

Protective colloids, 16, 18.

Pseudo-solution, 4.

Purple of Cassius, 55.

Q

QUINCKE, G., 95.

R

RADIUM emanation, 100.

Raffo, M., 51.

Raoult, Laws of, 81, 82, 92, 93.

Reducing agents, 64, 66.

Relation of colloidal solutions to solutions proper and to suspensions, 20.

Research methods, 71.

Richter, J. B., 52.

Ritter, J. W., 67.

Rose, G., 7.

S

SABANEJEW, A., 81, 82.

Salts, 34, 35.

Schneider, E. A., 40, 51, 55, 56, 57, 63, 88, 93.

Schulze, H., 17, 46, 47, 48, 52, 88, 90.

Schwellenwerte, 17.

Scum or cream formation, 12.

Sedimentation, 12.

Selenium, 52.

Sewage purification, 105.

Siedentopf, H., 22, 76, 100.

Silicic acid, Colloidal, 3, 37.

Silver, 59.

Size of particles, 78.

Sols, 4.

Solutions, 20.

Solution theory, The, 80.

Spark length, 70.

Spectrum analysis, 28, 72.

Spring, W., 21, 46, 49, 90.

Stannic acid, 45.

Starches, 12, 25, 26.

Substances known in the colloidal state only, 35.

Sulfogel, 15.

Sulphides, 34, 46, 50, 98.

Sulphur, 51.

Summary of matter known in the colloidal and crystalloidal states, 33.

Surface development, 5, 86.

„ tension, 84.

Suspension colloids, 30.

Suspensions, 24.

Suspension theory, The, 88.

Suspensoids, 30.

Svedberg, The, 14, 29, 69, 70, 71.

Swelling, 5, 8, 93.

T

TAMMANN, G., 92.

Tannic acid, 8, 92.

Thorium hydroxide, 43.

Thunderstorms, Effect of, 50.

Titanium hydroxide, 43.

Transformations, 14.

Transition stages, 22, 23, 26.

Traube, J., 84.

Tungstic acid, 43.

Tyndall effect, 12, 71.

U

ULTRAMICROSCOPE and ultra-microscopy, The, 12, 21, 27, 28, 30, 31, 71, 87, 96.

V

VALENCY of the kation, Effect of, 95.

Van't Hoff, J. H., 81.

Vapour pressure, 85.

Vegetable parchment, 2.

Velocities of diffusion, 8.

Viscosity, 30, 31.

W

WANDERING of particles, 94.

Wehnelt interrupter, 70.

Weimarn, P. P. von, 5, 28, 30, 95, 96.

Wiedemann, E., 83.

Winkler, Chl., 58.

Winssinger, 50, 90.

Wöhler, F., 59.

Wright, L. T., 48, 88.

Z

ZSIGMONDY, R., 9, 18, 21, 22, 45, 46, 53, 54, 56, 57, 58, 74, 75, 77, 80, 83, 95, 96.

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